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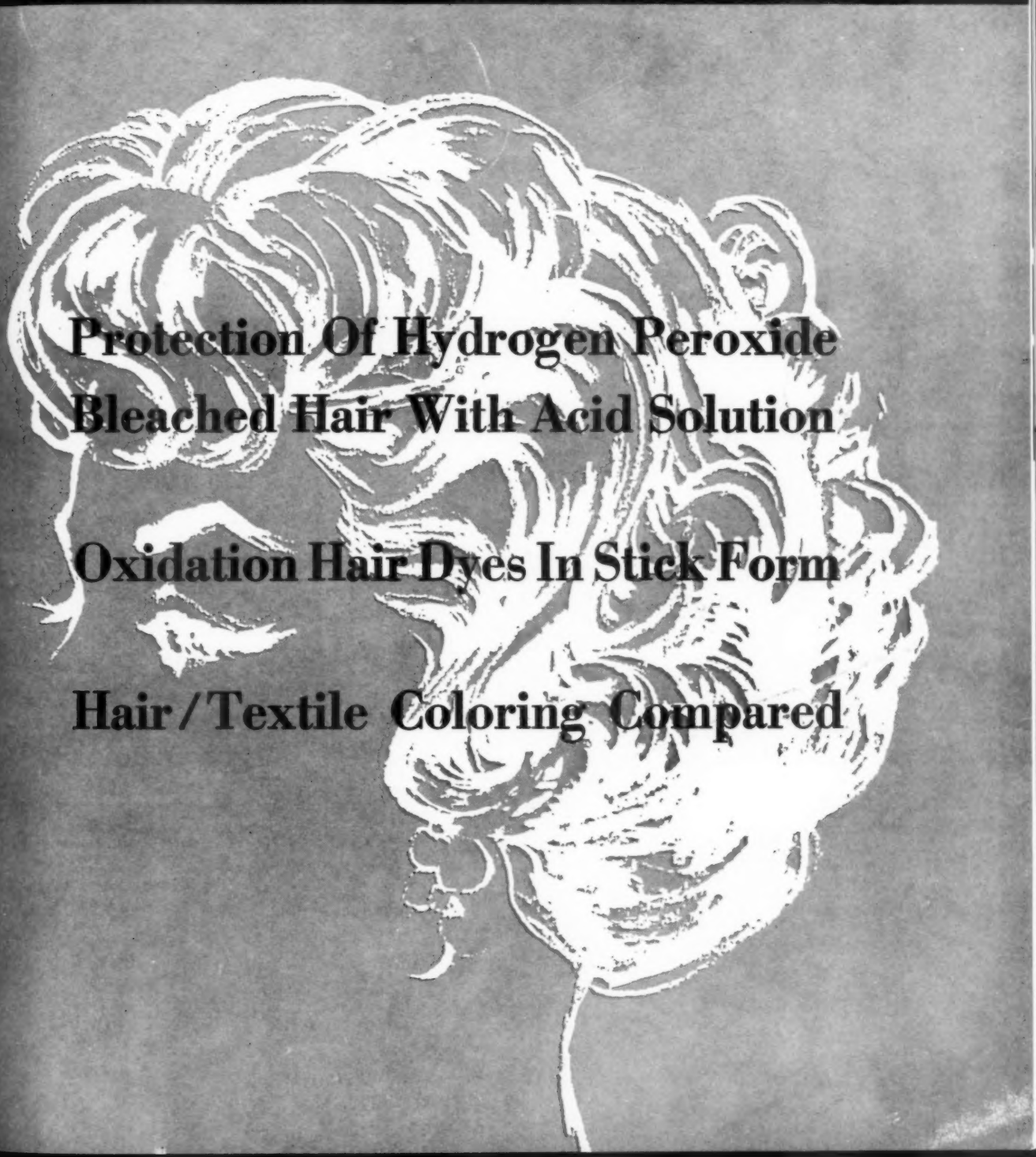
MAY 1960

THE MAGAZINE OF TASTE AND SCENT



Protection Of Hydrogen Peroxide Bleached Hair With Acid Solution

Oxidation Hair Dyes In Stick Form

Hair / Textile Coloring Compared

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American Perfumer
AND AROMATICS

VOL. 75, NO. 5 MAY, 1960

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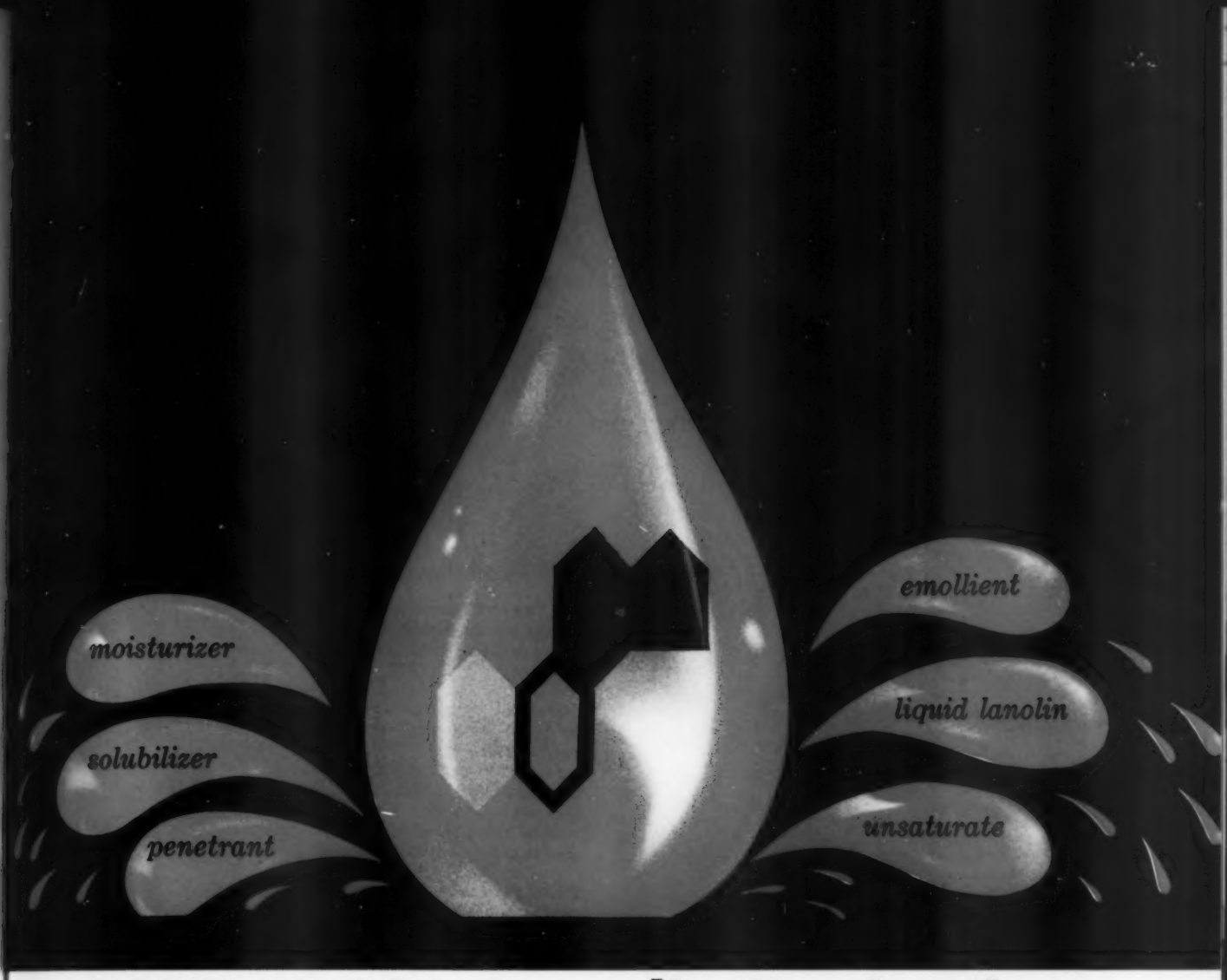

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LAST MINUTE NEWS . . .

New technical director at Toni Company

Dr. Ray C. Houtz, formerly laboratory director of The Toni Company division of The Gillette Company, has been appointed to the new post of technical director. Dr. Houtz joined the company in 1954 as director of basic research and service operations. Herman Bogaty will succeed Dr. Houtz as laboratory director.

National Healthaids changes name to Sulray, Inc.

National Healthaids, Inc., Tuckahoe, New York, producers of medicated cosmetics and drugs, has announced that they will now be known as Sulray, Inc. Hal A. Salzman, president, has announced that coincident with the name change national distribution of the company's newest product "Blem-Stick" will be achieved. The new product, an acne hinder-healer, is added to a line consisting of Sulray Sulphur Baths, Sulray Colloidal Sulpher Soap, and 7-Day Clear. Seven additional medicated cosmetic and drug items will be introduced later in the year by Sulray and its sister corporations: Otis Laboratories, Clay Franklin and Hallmark Laboratories.

Alberto Culver opens new plant

A new structure containing facilities for offices, laboratory, manufacturing and warehousing has been opened by the Alberto Culver Company in Melrose Park, Illinois. The million dollar building contains a small theatre with a seating capacity of one hundred people where the company plans to hold live demonstrations of the company's products.

Culver's products include Rinse Away, VO-5, Command and Tresemme, all hair care items. Intensive television promotion of the firm's products accounts for an annual advertising budget in excess of ten million dollars making them one of the largest users of this medium in the United States.

The firm moves to the new plant from 4201-19 Grand Avenue, Chicago.

New aerosol filling plant opens in Cincinnati

Cincinnati Aerosol Corporation is now in operation at 125 Terrace Drive in Cincinnati, Ohio, for custom and contract aerosol filling. Initial production facilities are capable of filling 432,000 units per week and will handle all types of filling except foods and pharmaceuticals. This type of filling, however, will also be done by the company at a later date. David T. Stebbins, president, states that the plant was opened to service manufacturers in Ohio, Kentucky and Indiana but future plans call for expansion into the national field where they already serve companies who do not have the facilities for aerosol filling.

Yardley constructs Los Angeles warehouse

Yardley of London, Inc. has opened warehouse facilities in Vernon, California. The building contains 18,000 square feet of floor space and was erected to expedite service to Yardley retail customers on the west coast and in the mountain states area. The address is 2535 East 28th Street, Vernon, California.

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Questions and Answers

Q. *Will you please suggest formulations for the followings.*

1. *A complete line of Negro hair preparations.*
2. *A complete line of Negro facial creams and lotions.*
3. *A cream preparation to be applied to a person's hands before exposure to grease and grime for protection. One that will wash off easily with ordinary soap and water.*

Thank you for your cooperation. I enjoy your publication very much and have learned a lot from reading it thoroughly each month. C. L. E., Georgia.

A. To send you formulations for a complete line of Negro hair and facial preparations is such a mammoth order that it would take a book of written material to give you the complete story. We cannot help but feel that you should consult someone acquainted with this type of manufacturing and pay them for developing the necessary formulas for you. If you have been a regular reader of the AMERICAN PERFUMER, you will have found stories as well as questions and answers on this subject from time to time. If you go back over some of the previous issues, you will pick up a few bits of information on this subject. As for the formulation of a protective preparation such as you describe, keep in mind that these products are formulated specifically for the type of protection that one has in mind. If it is to be against grease and grime, that is one thing. If it is to be against something else, that is different. A product that protects against grease and grime is the standard vanishing cream formula in which the amount of soap is approximately double what it ordinarily would be. That means that from 30 to 50 per cent of the stearic acid used in the formula should be saponified with an appropriate alkali so that it leaves a soluble film on the skin. This film is not generally permeated by grease and enables the grease to be readily washed off afterwards. The addition of a gum 0.1 to 0.25%, such as methyl cellulose enhances protection against grease.

Q. *As a reader of your magazine, we wish to know the supplier of the applicator used in the "Odo-Ro-No Satin Sponge Liquid Deodorant. P. B. D., Denmark*

A. You might try the following three companies for applicators used in liquid deodorants:

Plastic Assembled Products Co.
1149 Watson Street
Baltimore 2, Maryland

Armstrong Cork Company
Lancaster, Pennsylvania

Glass Products Company
Vineland, New Jersey

We regret we are unable to give you the exact supplier of this type applicator in the product mentioned, since we do not know who makes it.

From time to time suggestions have been and will be made in this magazine with respect to processes, devices, materials, appliances, equipment and the like. It is not practicable for the writers and editors to have a patent search or examination made in connection with each such suggestion. Our readers are, therefore, requested and indeed urged to determine for themselves whether any patent or other right will be violated before acting on any such suggestions.

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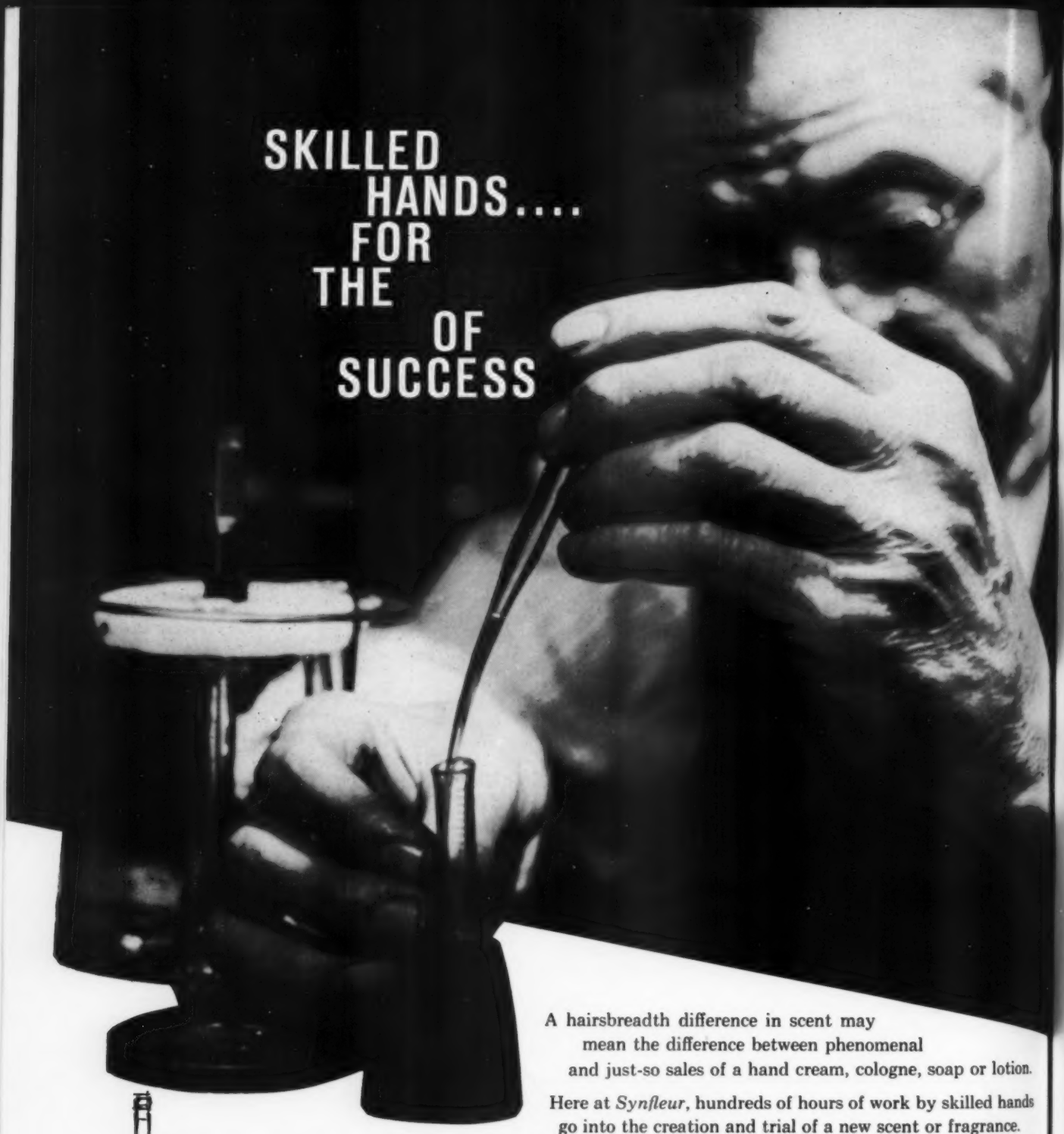

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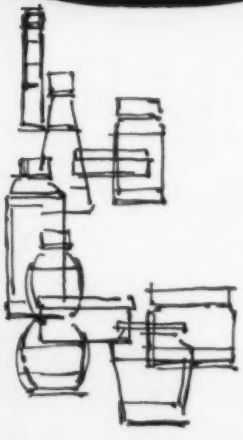

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DESIDERATA

Maison G. deNavarre, M.S., F.A.I.C.

Panthenol Lipstick

Several hundred people heard the Magid et al paper on the use of panthenol in cosmetics when it was delivered before the T. G. A. Scientific Section. Hundreds of others have since read it. The application to lipstick sounded interesting enough to give it a try.

But there is a rub. Panthenol is not soluble in the usual lipstick fats and waxes. It stays as a glob at the bottom of the mixing container.

Off went a letter to Dr. Louis Magid at Hoffmann-LaRoche, Inc., Nutley, New Jersey, with a quick reply from him which has been authorized for publication in case others had the same trouble. We will avoid the quotes but all the following is direct from Dr. Magid.

> Concerning the incorporation of panthenol into lipsticks, the finished product represents a fine dispersion of the panthenol in the lipstick ingredients, since panthenol is not soluble in fats and oils. The incorporation of the panthenol, butyl stearate and isopropyl myristate mixture is facilitated by warming to about 65°C, the panthenol being further dispersed upon mixing with the melted fats and upon the addition of the pigments and subsequent mixing. More suitable methods for you in incorporating the panthenol may be one of the following:
>
> (1) Solubilization of the panthenol in the alcoholic perfume mixture and dispersion of this mixture in the castor oil or the melted lipstick base in the same manner as the perfume.
>
> (2) Solubilization of the panthenol with alcohol in the ratio of approximately 3 parts to 1 part, respectively. This mixture can be dispersed in the lipstick base in the same manner as the perfume.
>
> (3) Dispersion of the panthenol (previously diluted with alcohol) on part of the pigments, such as titanium dioxide with subsequent drying and incorporation of the mixture into the melted lipstick base.
>
> (4) Addition of the panthenol directly to the melted mixture of fats, waxes and castor oil with subsequent mixing. Upon addition of the pigments and further mixing, the panthenol will be uniformly and finely dispersed.

For further information write

Swiss Honors

A cablegram received on March 26th from Bern, Switzerland reads as follows:

> "For his contribution to cosmetic science and his work for the International Society Mr. M. G. deNavarre is today elected Honorary Member of the Swiss Society of Cosmetic Chemists."

To this I replied:

> "J'accepte votre honneur par cablegramme avec grand plaisir. Une lettre suivrai."

(Hope my French was O.K.)

I am everlastingly indebted and forever grateful to my Swiss contemporaries for the distinction of being their first Honorary Member. I hope to say this to them personally this August when the S.C.C. again makes its tour of European Seminars.

Dr. Magid in the Fine Chemicals Division.

Notes

Freddy Wells and friend Littlejohn had a chance to see a lot more of each other at the opening of the Bergamot Consortium at S. Gregoris, Calabria. (Freddy must tell me again about a similar trip he made a couple of years ago. Statements from others and those from Freddy don't add up.) Among the others present were J. Hackforth-Jones and J. H. Seager of Yardley; Misters E. A. Diamond and C. C. Pryor of Unilever; Marcel Schwob; Arnold Munns and the ever present Dr. S. Sabetay. . . .Did you know that a powdered form of Veegum is also available. The flake being the usual grade. . . .Sure get a kick out of the way the "drug" store operators especially in Canada are battling direct selling companies on vitamins. It seems they think these companies should stick to their main lines such as cosmetics and household specialties. Of course it is O.K. to sell toys, chairs, flowers, hardware and the like in a "drug" store. . . . .And while in the whudunit vein, OH! Fidel, wherefore art thou going with that lovely island. . . .Have just seen some samples of powdered synthetic resin foam being offered in Europe as a powder base. Sure is white and adheres well. . . .It is a sad state of affairs when a Congressman can force legislation by a threat such as "No cancer clause, no new law." We all know that election year is here, but Oh, for a little sanity. . . .Possibility of some new taurates being available for shampoo use if there is a market. Haenni and Hall (JAOAC *43*, 92, 1959) are using U.V. to determine the aromatic content of mineral oils used in food processing. An U.V. limit of 0.5 in a 0.1 mm path at 270 mu is the criterion used and oddly enough a number of U.S.P. oils exceeded this figure significantly while some non U.S.P. oils were under. . . .Wonder why lithium or strontium thioglycolates should act differently from sodium, ammonium or calcium thioglycolate, if they do. . . .Dihydroxyocetone, the tanning ingredient of a certain after shaving lotion that gives a Carribbean tan at home etc., is being made by fermentation at a really interesting price, but more on this later. . . .The Detroit News of February 24th carried a story on a new toothpaste factory going up in Singapore costing $400,000. They are to make the usual toothpaste and some very unusual ones flavored with banana, pineapple and durian no less. The average occidental doesn't know durian. It has been described by one writer as "rich butter-like custard, highly flavored with almonds." Others liken it to a mixture of onion and camembert cheese. This king of fruit as sold in the orient causes the novice to hold his nose when whithin ten feet of a durian fruit stall. The advertising slogan states the Detroit News, might be "Can you endure your teeth today". . . .The February issue of CHEMICAL PRODUCTS (British) has one of the best summaries on aerosol production I have seen. Lists brand names, use, active ingredient, propellant, valve and container type as sold in the U.K.

More Notes

Flemming cancer scare regarding cranberries containing aminotriazole may show it up as a treatment for an overactive thyroid according to the March 19th issue of the J.A.M.A. . . . .the same issue carries a story by Macdonald, Chairman of the A.M.A. Subcommittee on Breast and Genital cancer, the press release of which is titled "Statistics Prove Sex (the release says 'Six') Hormones AID Victims of Breast Cancer." . . . .In case you are interested in attracting melon flies, Beroza and Corvorkers (SCIENCE *131*, 1044, 1960) find that 4-(p-acetoxyphenyl)-2 butanone is superior to anisylacetone, up to now considered the best. . . . A nonsteroidal androgen has been reported by Dorfman (SCIENCE *131*, 1096, 1960) as being a 2-acetyl-7-oxo-1, 2, 3, 4, 4a, 4b, 5, 6, 7, 9, 10a-dodecahydro-phenanthrene. . . . Charabot's Nouvelles de Grasse for Feburary, 1960 points out that only **trans** anethole exists in natural oils of aniseed and fennel; synthetic anethole is a mixture of **cis** and **trans** forms. The **cis** variety has been shown to be toxic. . . . The overseas Post for January, 1960 has an interesting article on spray dried drug extracts. . . .In the same issue is a description of a new German drug containing among other things Sabal serrulata claimed to be "a specific for hypertrophy of the prostate, its chief effect being that of decongesting the adenoma." . . .Some people feel that if an ingredient is useful in one medium it works in all, witness the inclusion of placenta in a soap made in France. . . . .

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American Perfumer
AND AROMATICS
May, 1960 Volume 75—Number 5

Oxidation hair-dyes in stick form

By Dr. R. Heilingotter

The possibility of using oxidation dyes for coloring human hair was first discovered by Monnatl. His method is still in use today because an equivalent one that could be handled as simply giving in so short a time at body temperature such good coloring results, could not be found.

In the beginning only the aromatic diamine p-phenylendiamine was used, but later on other diamines, aminophenols and finally also aromatic nitrocompounds have been used together with colour stabilizing additions (2). In some countries p-phenylendiamine has been replaced by p-toluylendiamine because of laws prohibiting the use of p-phenylendiamine in cosmetics. In the United States this base is still admitted but its use is restricted by the warning to do a preliminary skin test before use and the so-called "may cause blindness" legend.

Both diamines are affected by the same peculiarity to produce allergic reactions on sensitive human skin. Experiences have shown that such undesirable accidents can be mainly eliminated by the use of purest starting materials and by observing the preliminary skin test and excluding allergic persons. The cream hair-dyes, today mostly in use, based on emulsions with fatty alcohols or glyceryl monostearate esters, or other suitable emulsifiers, are less dangerous. The percentage of allergic accidents is estimated at 0.0001 to 0.0002 percent by Wilmsmann (3). He believes that such emulsion systems retard the penetration of the dyes into the skin.

Formerly only aqueous solutions were manufactured as liquid hair-dyes, but later on more heavily bodied preparations have been preferred because of their better practical qualities. So, dyes based on liquid soap, with or without addition of turkey red-oil, on pure red-oil base (4), on base of jellys (6) using methylcellulose, carboxymethylcellulose, gum traganth (8) or polymethacrylates. Lately a revolutionary way has been discovered by Stroher (9) using creams as base of hair-dyes. In such preparations the colouring active ingredients are dissolved in the aqueous phase of an oil/water-emulsion, using high molecular aliphatic alcohols, such as cetyl-stearyl-alcohol, or glyceryl monostearate esters as emulsifiers, with other fatty compounds and suitable detergents. It was surprising that the oil phase did not affect the dyeing process, although at this time oil and fatty residues on the hair were considered as unwelcome and were carefully removed before dyeing. Today cream hair-dyes are dominating the market.

After having endured all changes, from liquid to viscous, from jelly to creamy consistency, only a solid product in form of a stick remains to be considered. It is obvious to think of dissolving the dyestuff in a watersoluble, viscous substrate, i.e. in soap. It seems to be the simplest way to mix the dyestuffs and the other ingredients with powdered soap, to press this mixture into bricks and to then cut them into bars or sticks (10). This method needs suitable machinery.

A similar way was described some years ago, by Huffmans (11).

Another way to manufacture such hair-dyeing sticks is by a simple melting process and casting into moulds, (12) by using semifatty bases, such as high molecular fatty alcohols and others, in which the dyestuffs are incorporated by melting and solubilizing.

Schwarzkopf too, besides using fatty alcohols as carrier for the oxydation dyestuffs, used for the same purpose, waxy appearing bases, such as polyoxyethylencompounds, glycerol stearates, alkylolamides of fatty acids and other products (13).

In manufacturing hair-dyes the diamines are always used in the form of their stable sulphates and the active base is separated from the salts during manufacture by addition of aqueous ammonia; in all these cases p-toluylendiamine or p-phenylendiamine comes into action as an aqueous solution.

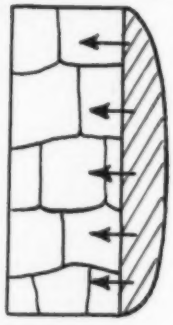
A solid dyeing stick, based on fatty alcohols, is not compatible with water because the forming of soft emulsions is then inevitable. The diamine cannot be incorporated as aqueous solution and inevitably separates as the free base.

If a good penetration of the hair-dye into hair keratine is to be obtained, a pH of at least 10 must be produced. In the case of a liquid hair-dye this is realized in a simple manner by the addition of ammonia. For the same reason mentioned above ammonia cannot be used and has to be replaced by an organic base, such as monoethanolamine, which must be able to dissolve in the stick base.

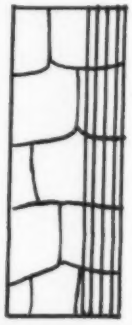
Considering the numerous components which comprise the stick it is necessary to choose such materials which will harmonize and be homogeneous. If a fatty alcohol alone, or mixed with other fatty or semifatty

Comparative outline of the dyeing process of human hair by means of (A) liquid, jelly or soap based hair-dyes, (B) creamy or pasty hair-dyes and (C) hair-dyeing sticks based on semifatty or fatty materials.

Fig. 1. Liquid or jelly dyes, also dyeing sticks by Clairol, based on soap.

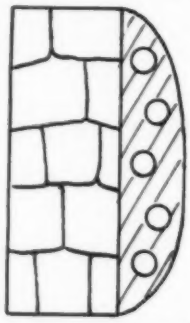


1a) Application: The dyestuffs are present in water solution or in a water soluble form, able to come immediately in contact with the hair.

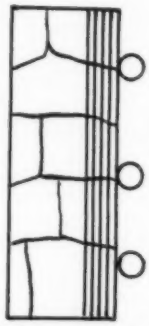


1b) Result: Hair-dye has penetrated directly into the hair; an intensive hair colouration has taken place.

Fig. 2. Creamy hair-dye, present as an oil/water-emulsion, by Stroher.

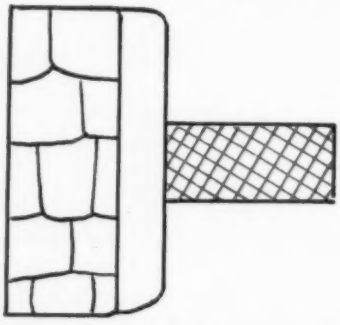


2a) The dyestuffs are dissolved mainly in the aqueous phase of an oil-water emulsion and are able, being the outer phase, to penetrate immediately into the hair.

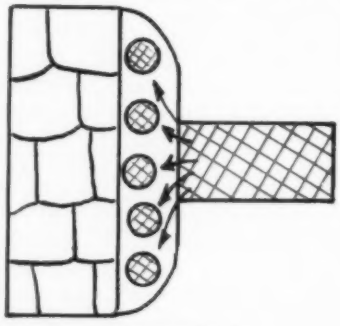


2b) An intensive hair colouration takes place; some fatty droplets are remaining superficially on the hair cuticula after dye has been removed.

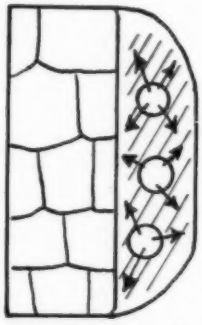
Fig. 3. Solid hair-dyeing stick by Heilingotter or Schwarzkopf.



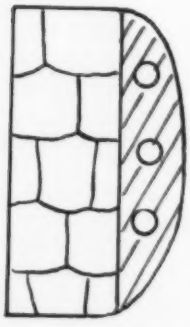
3a) Application of the hair-dyeing stick to hair, wetted by diluted hydrogen-peroxide solution.



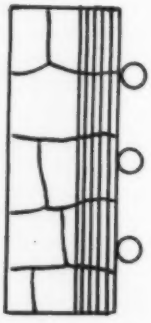
3b) Separation of dyestuffs containing semifatty droplets by emulgation; the aqueous phase contains no colouring matter.



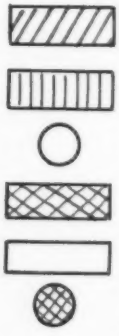
3c) Diffusion of the dyestuffs from the fatty phase into the water phase takes place.



3d) Diffusion is carried out, hair stands in immediate contact with a colour containing solution; an intensive hair colouratakes place.



3e) After dye has been removed hair is dyed deeply; fatty droplets are remaining superficially on the hair cuticula.



Aqueous solution of dyestuffs or a colouring matter containing water-phase of an oil-water emulsion.

Dyed area of hair.

Semifatty or fatty droplets.

Hair-dyeing stick.

Hydrogen peroxide solution adherent on hair.

Dyestuff containing semifatty or fatty droplets.

products, is used, the predominant question is that of the solubility of the dyestuffs. With the aid of suitable solubilizing agents it will dissolve the most important oxidation dyestuffs. Materials causing difficulties, must be replaced by others.

To obtain the necessary alkalinity, monoethanolamine is suitable, but special tricks must be used to produce a pH above ten.

For the reason that oxidation dyestuffs are sensitive to oxidation and can easily become ineffective, the addition of an antioxidant is necessary. The usual alkali sulphites cannot be used because of their insolubility in fatty materials; suitable organic compounds, such as monoethanolaminesulphite, must be used.

To prevent oxidative decomposition during storage caused by the presence of catalytic metal traces in the technical raw materials, a sequestrating agent must be dissolvable in the stick. It is also necessary to provide the sticks with an impermeable coating, i.e. of paraffin, to obtain long shelf life; this coating has to be removed on one side, before use.

Further, a detergent is necessary to facilitate the transformation of the stick on the wet human hair into an emulsion. The detergent may not be suspended in the stick-base; it must be dissolvable therein.

Finally a stick must be produced which is not only homogeneous when melted, but which does not separate liquids, after congealing. Since a great number of components go into the final composition, it follows that it may not be so easy to produce the necessary homogenity.

Taking into consideration the quality of the final hair-dyeing stick, the composition of the basic compound is of great importance. The materials used must be chosen in such a way, that shrinkage and the forming of a middle vortex in the stick, must be prevented as far as possible. The sticks must be so hard that a suitable usability is guaranteed; they must not be too hard and not too soft, but must correspond to a consistency which allows them to pass easily and softly over the hair. Finally, stick composition must be chosen in such a way, that the melting point lies somewhat above 40°C. For tropical climate the composition of the stick has to be another than for countries with moderate climate.

Oxidation hair-dyes are only able to dye the hair, if they are used together with an oxidizing agent, mostly with hydrogen peroxide. Therefore, all hair-dyes must be mixed in adequate parts with a diluted hydrogen peroxide solution before use.

After application of a hair-dye on the hair, a swelling occurs by the action of the alkalinity and at the same time a penetration of the dyestuff containing phase into the hair begins. Simultaneously a slow oxidation reaction takes place, whilst high molecular oxidation products, (pigments) are formed. The oxidation reaction proceeds slowly, but is completed, nevertheless, in 15 to 25 minutes. The formed colors are anchored in such a manner in the hair-keratine, that the dye cannot be removed and the hair coloration is then stable against water and shampoo treatments. It also has sufficient light stability.

Solid hair-dyes cannot be mixed with hydrogen peroxide before application. In this case the hair must be moistened with hydrogen peroxide solution before the application of the stick.

In all oxidation hair-dyes, whether liquid, viscous, jelly-or creamy consistency, the coloring active components are present in aqueous solution or in an aqueous phase of an oil-water-emulsion. By application to the hair they are able to come immediately in contact with hair to be dyed. Penetration of the aqueous medium into the hair can proceed without any hindrance. By the use of cream hair-dyes an absorption of dyestuffs by the fatty phase takes place to a slight degree, but the main part remains in the aqueous phase and is able to directly penetrate into the hair. See fig. 1 and 2.

This is not the case with solid hair-dyeing sticks, based on fatty alcohols, semifatty compounds or similar compositions. In this case, the dyestuffs are exclusively dissolved in a fatty medium. Fig. 3a. By application on the wet hair, the colour containing fatty medium is dispersed in water and these fatty particles stay in an aqueous colorless medium, so that the dyestuffs have no possibility of entering the hair-keratine. A coloring of the hair is not to be expected. Fig. 3b.

But suddenly after dispersion of the fatty particles by emulsification a surprising penetration of the dyestuffs into the aqueous phase takes place. Fig. 3c. This diffusion process takes place in such a quick manner, that the aqueous phase is provided with coloring material in a short time, enabling it to penetrate into the hair without delay. Fig. 3d. The hair-dyeing process is then carried out in the same quick manner as by application of the ordinary aqueous hair-dyes. Fig. 3e.

The intensity of the colorations that may be realized with oxidation hair-dyes depends in a high degree on the concentration of dyestuffs. Concentrated color solutions in general lead to dark colorations; less concentrated solutions to lighter shades. The ratio between dyestuff and water is exactly determined for each shade. By using solid hair-dyeing sticks this proportion is not as easily maintained. It is possible to provide the sticks with a definite quantity of dyestuffs, but the water content on the hair cannot be exactly controlled. Shade is also dependent on whether the stick passes only softly over the hair, or whether manipulation is repeated frequently. Therein lies a certain uncertainty but practice has shown, that by using uniform techniques shade differences are rarely encountered and sufficient dyestuff can be emulsified in the occluded water volume on the hair by carefully stroking the coloring stick over the hair.

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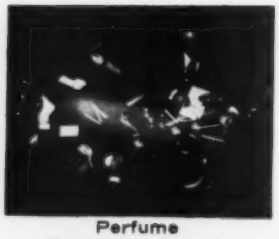

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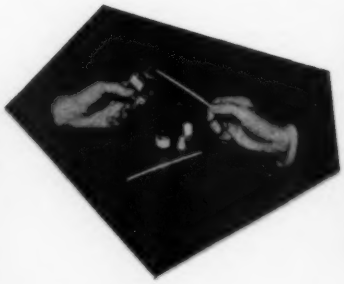

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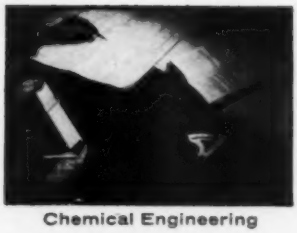

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Protection of hydrogen peroxide bleached hair with acid solutions

By Peter Flesch, M.D., Ph.D.

BLEACHING of hair with hydrogen peroxide damages the hair shaft. The hair may become dull and brittle, often takes up dyes in a rapid and irregular way and is especially vulnerable to thioglycolates (1). The objective signs of the damage are disruption of the normal cuticular pattern, changes in load extension curves (2, 3), increased permeability of the hair shaft to radio-active detergents (4) and profound alterations in the chemical composition and behavior of the hair (5-10). Although a great deal of work has been done in this field, especially in the wool industry, the exact nature of the damage is unknown and no methods are available to protect the hair against the deleterious effects of hydrogen peroxide.

In the course of dyeing hair by combining thioglycolate with certified hair dyes (11, 12) it was found by cosmetic chemists that these otherwise satisfactory dyes caused considerable damage to hair which had been bleached previously. The hair shafts became brittle, matted and badly discolored in an irreversible way. In an attempt to prevent this damage, I have found that certain organic acids offered a large measure of protection against the injurious effect of the combined hair dyes, provided that these acids were applied to the bleached hair prior to the dyeing process. It soon became apparent that this protective effect was purely a function of the pH of the solution: any acid solution was equally effective in protecting the hair against many of the harmful consequences of the bleaching process, if its pH was between 2.0 and 3.8.

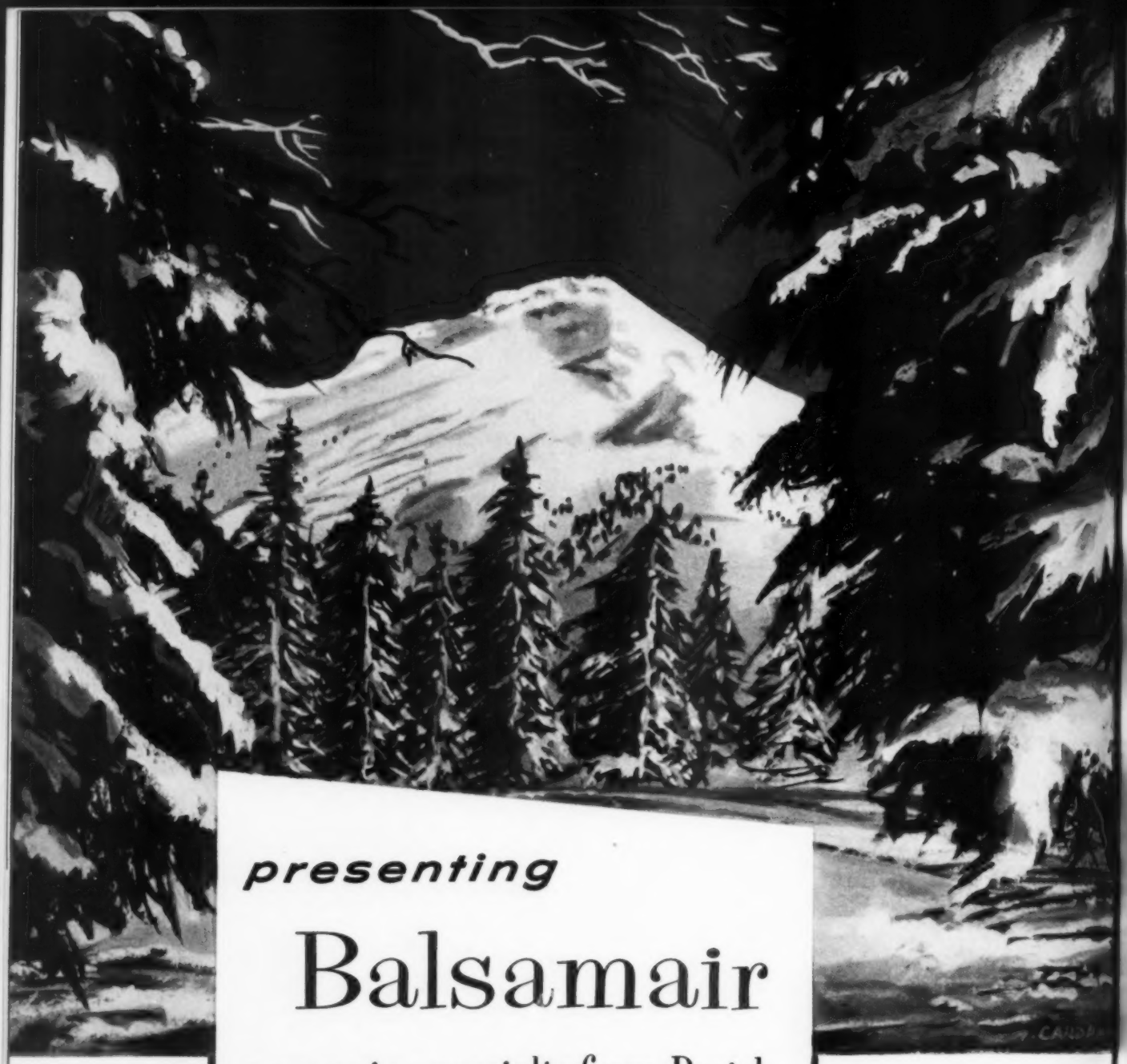
The present work deals with the nature and basis of this protective effect, and with the general implications of this new finding. Detailed experimental data will be published in a later report.

Materials and methods

1—Bleaching of human hair with hydrogen peroxide. In studies with bleached hair, several precautions must be taken. In the first place, commercially available bleached hair is unsuited for many experimental purposes. The way in which such hair is bleached is generally unknown. A more serious objection against its use is that commercial bleached hair is subjected to thorough washing, a treatment which rarely reproduces the conditions under which human hair is bleached in everyday life.

A second point to keep in mind is that there exists no real standardized method of bleaching human hair. Penetration of peroxide into the hair shaft is influenced by the thickness of the hair and therefore variations in the reactivity of different hairs toward peroxide are pronounced.

In our work we accomplished standardization of the bleached hair in two ways. For chemical studies we pulverized the hair before or after bleaching in a Wiley mill or Waring blendor (13). Hair powder has the advantage over whole hair of being more accessible to bleaching and to extraction with various solvents. The objection that it is an artificial product can be overcome by checking the experimental findings against whole hair. For load extension studies we divided individual hairs into small sections and com-



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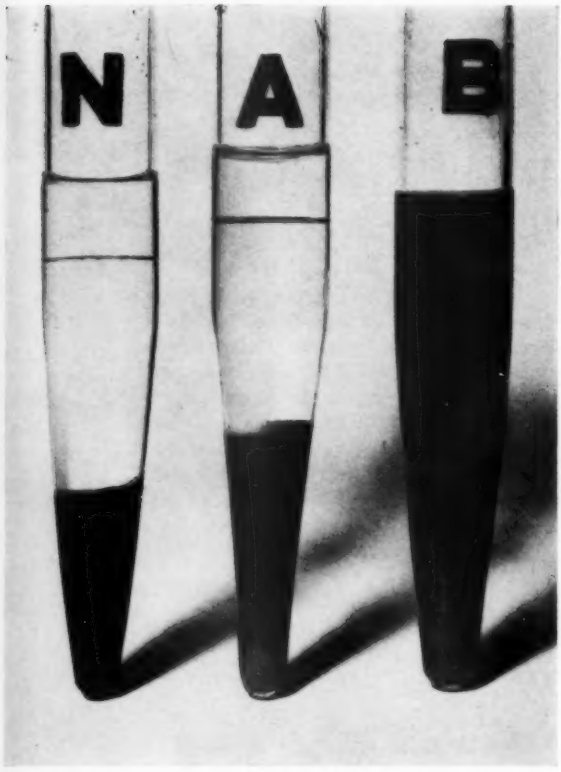

Figure 1—Hair powders incubated with Orange II. N: unbleached hair. A: acid treated bleached hair. B: bleached hair, not treated with acid. Both unbleached and acid treated bleached hair combine with the dye.

pared the effects of different agents on the individual sections. In this way an individual hair shaft served as its own control.

Hair was obtained through the courtesy of barber shops. The hair was cleaned with several washings of chloroform and ether and dried at room temperature. Bleaching was carried out at room temperature over 2 to 30 minutes with hydrogen peroxide (30%) diluted with 2 to 4 volumes of water to which a few drops of ammonia have been added. The hair then was washed several times in running distilled water for brief periods and dried before further testing.

2—Treatment of bleached hair with solutions of varying pH. For the sake of uniformity, the hair was treated with buffered solutions at room temperature for 10 to 20 minutes. The acid buffers used were 1% potassium phthalate-tartaric acid buffers of pH 2.0 to 3.8 and HCl-glycocoll-NaCl buffer of pH 3.33 (Hartmann-Leddon Company); the more neutral buffers were 1% phosphate buffers. The hair was then washed with water until the washings gave a neutral reaction.

3—Tests for characterizing bleached hair. Tests for the identification of peroxide treated hair are based on the oxidation of the disulfide linkages in keratin to various sulfur-oxygen combinations (R-SO-S-R, RSO_2-S-R, R-SO-SO-R, R-SO_2-SO-R, R-SO_2-SO_2-R) (6) and on characteristic reactions given by some of these oxidation products.

(a) The iodine test is due to the oxidation of the iodide ion to free iodine by cystine disulfoxide present in the bleached hair:

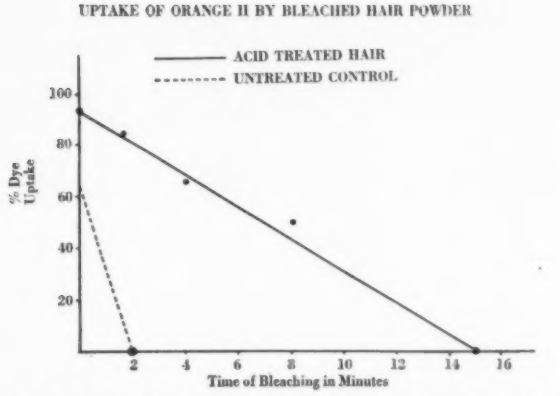

Figure 2—Orange II. uptake by bleached and acid treated bleached hair powder under extreme conditions of bleaching. (30% H_2O_2, 25% ammonia water).

$$R\text{-}(SO)_2\text{-}R + HI \longrightarrow R\text{-}S\text{-}S\text{-}R + 2\ I_2 + 2\ H_2O \quad (7)$$

(b) The lead sulfide test is negative in bleached hair in a pH range where it gives positive results with unbleached hair. The chemical reactions of unbleached hair involved in this test are: (6)

$$R\text{-}CH_2\text{-}S\text{-}S\text{-}CH_2R \underset{\text{Decreasing pH}}{\overset{\text{Increasing pH}}{\rightleftharpoons}} RCH_2SH + RCH_2SOH$$

$$\text{pH Incr.} \downarrow\uparrow \text{Decr pH}$$

$$PbS \xleftarrow{PbAc} H_2S + RCHO$$

(c) Both the iodine and lead sulfide tests are qualitative. A third test, the Orange II test gives quantitative data, by permitting the accurate estimation of the uptake of the acid dye, Orange II. Only unbleached hair combines with this dye (8). In our modification of the test, hair powder, as well as whole hair was used and the hair was incubated with the dye solution for at least 24 hours at 50°C.

4—Load extension studies. Stretching of the hair was carried out with an extension apparatus built from an analytical balance. A constant rate of loading was achieved by running a steady stream of water into a beaker which served as a counterweight to the hair that was being stretched. The extension of the hair was measured against a scale and expressed in percentages of the original length of the hair. In all cases sections of the same hair served as experimental specimens and their controls.

5—Chemical studies. Nitrogen, sulfur and phosphorus were estimated in bleached hair and in hair extracts. Sulfhydryl groups were determined with Bennett's reagent (15).

Results

1—Properties of bleached and acid-treated bleached hair. After bleached hair has been treated with an acid buffer of pH 2.0-3.8 for 10-20 minutes at room temperature, its behavior toward the identifying tests changes. There appeared to be a slight release of PbS, when the acid-treated bleached hair was immersed in boiling lead acetate and the liberation of free iodine from KI was less than in control specimens. Both these

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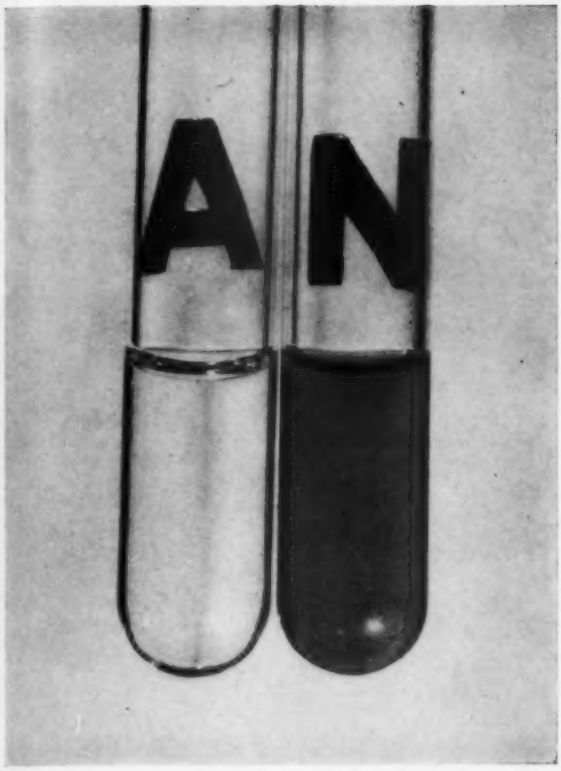

Figure 3—Extracts of acid treated (A) and neutral (N) bleached hair. The acid extract is colorless, the neutral extract colored and turbid.

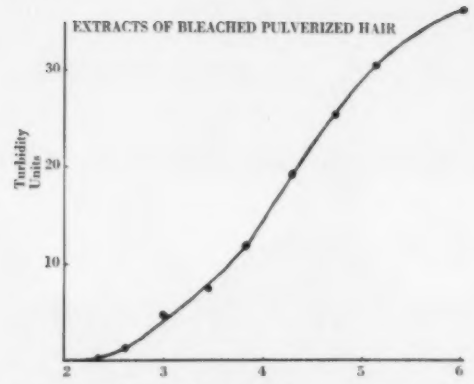

Figure 4—Turbidity of bleached hair extracts at various pH-s.

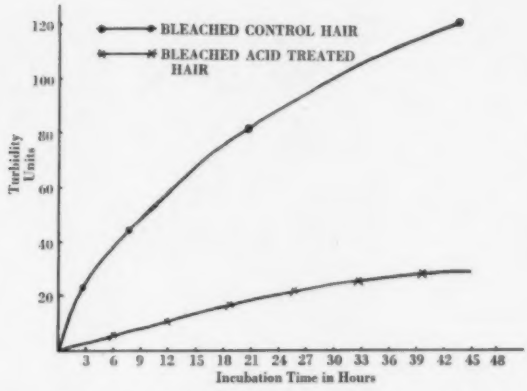

Figure 5—Turbidities of extracts of bleached hair, treated with neutral solvents and pH 3.4 buffer respectively.

tests are qualitative; we found neither of them pronounced enough to be of much value.

However, the results obtained with the Orange II test were consistent and quantitative. As in the other two tests, acid-treated bleached hair reverts to the behavior of unbleached hair, inasmuch as it combines rapidly with the dye. (Fig. 1.) The extent of the combination of the dye with the hair depends on the length of the bleaching procedure; the longer the bleaching process, the less the hair combines with the dye (Fig. 2).

It was observed that in the course of this reaction, the dye solutions which were incubated with bleached hair that had been treated with neutral solutions, became turbid, while the supernates of acid-treated bleached hair were clear. This observation had led to the following basic experiment. Bleached hair or hair powder was divided into two parts. One part was treated with an acid (pH 2-3.8) buffer, the other with a neutral buffer. After washing the hair free of buffer solutions, both portions were incubated with water at 36°C or 50°C for several hours. The extract of acid-treated bleached hair remained clear and colorless, or turned faint yellow; the extract of the "neutral" bleached hair became turbid and more or less colored, (Fig. 3). The turbidity of these extracts could not be diminished by repeated centrifuging or filtration.

The ability of aqueous solutions to extract from the bleached hair material which causes turbidity is a function of the pH. Below pH 3.6 the amounts extracted are negligible; they increase rapidly with a further rise in the pH (Fig. 4). Extraction occurs already after a brief period of incubation; in our experiments, half hour's incubation of the bleached hair with water at 36°C caused a measurable increase in the turbidity of the extract.

The protection afforded to bleached hair by acids against extraction by water is of long duration. A single immersion of the hair for 20 minutes in a buffer of pH 3.4 prevents the appearance of a significant turbidity in the extracting water for 12 hours (Fig. 5).

These experiments suggest that in the course of oxidation by peroxide some of the constituents of the hair become water-soluble. Upon exposure of the bleached hair to acid solutions, these components are precipitated within the hair shaft and cannot be extracted anymore. The presence of such acid-precipitable components in bleached hair may be demonstrated by treating the aqueous extracts of bleached hair with buffers of different pH. Precipitation occurs at all pH-s below 3.8. At pH 4.0 and above, the turbid extracts show no sign of precipitation (Fig. 6). On the other hand, in the extracts of acid-treated bleached hair, slight precipitation occurs at strongly alkaline reactions only.

The theory that acid treatment precipitates certain components within the bleached hair receives indirect support also from sulfhydryl estimations. Unbleached hair contains small, but appreciable amounts of sulfhydryl groups, (16) which are almost completely inactivated (oxidized) by hydrogen peroxide. When

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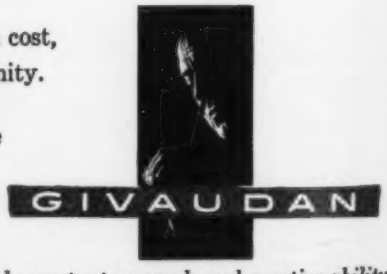

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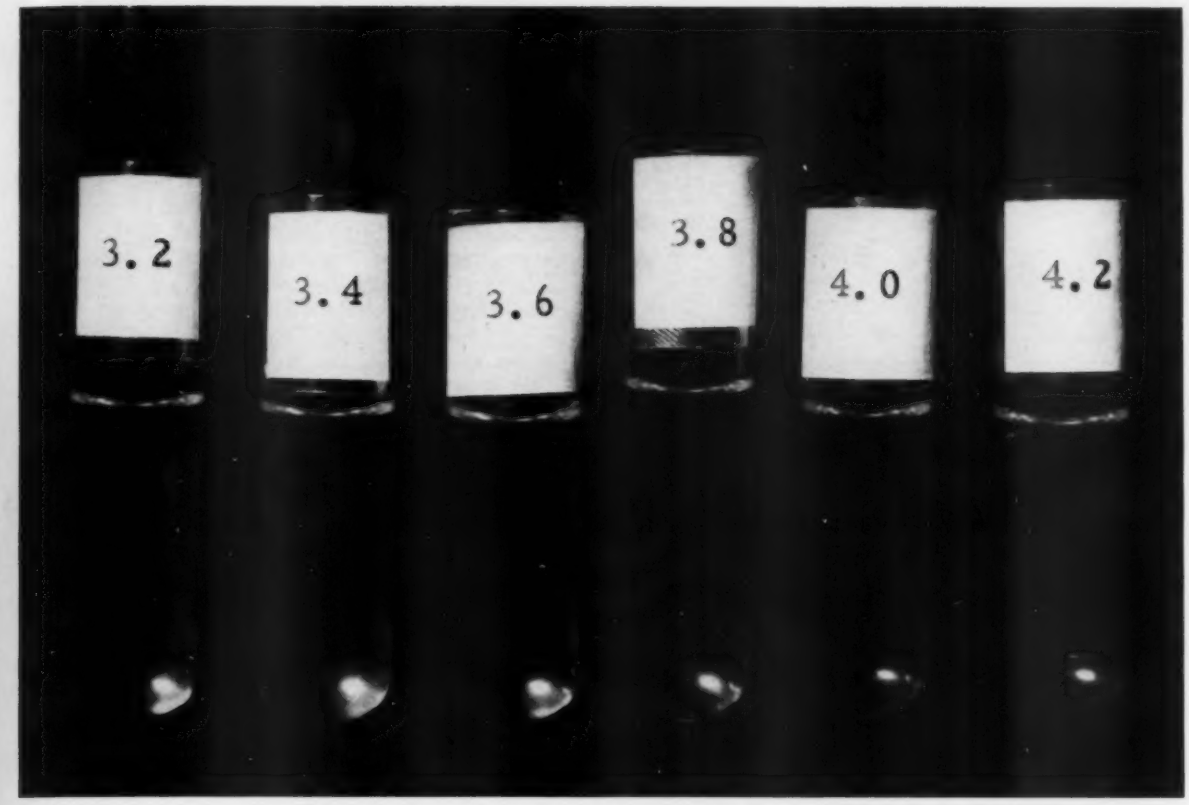

Figure 6—Precipitation in extracts of bleached hair in buffer solutions. Precipitation occurs up to pH 3.8.

TABLE I

Sulfhydryl contents of bleached hair powder treated with acid (pH 3.3) and neutral solutions.

	—SH in mMx10^{-2}/100 Gm	
	Acid treated:	**Neutral:**
Experiment #1 (½ hr. incubation with Duponol)	0.025	0.060
Experiment #2 (16 hrs. incubation with Duponol)	0.035	0.17

TABLE II

Nitrogen, phosphorus and sulfur contents of bleached hair treated with acid and neutral solvents and in extracts of these hairs.

	Nitrogen	Phosphorus	Sulfur
Neutral hair	14.30%	0.02%	4.89%
Acid hair	14.26%	0.11%	4.92%
Neutral hair extract	0.09%	Less than 0.01%	0.05%
Acid hair extract	0.08%	Less than 0.01%	Less than 0.01%

bleached hair is treated with acids, the last remnants of the sulfhydryl groups disappear (Table I). This phenomenon may be explained by assuming that precipitation within the hair shaft caused by acids encloses the remaining sulfhydryl groups and makes them unavailable for chemical analysis.

The nitrogen, phosphorus and sulfur contents of bleached and acid-treated bleached hairs and hair extracts are reproduced in Table II. Less sulfur and phosphorus are extracted from bleached hair which had been subjected to acid treatment than from hair treated with neutral solutions.

2—Load extension studies. A characteristic feature of the stretch curves of peroxide treated hairs is the partial or complete elimination of the first part of the curve (3). When stretched, the bleached hairs extend almost immediately. Acid treatment has no effect on this pattern.

When bleached hair is treated with thioglycolates, the third portion of the load extension curve becomes steeper as an indication of damage inflicted upon the disulfide linkages (17). Acid treatment of the bleached hair, prior to incubation with thioglycolates, reverts the load extension curve of the thioglycolate treated hair to the pattern of bleached hair that has not been subjected to thioglycolates (Fig. 7). However, when the hair has been excessively damaged by the combined actions of peroxide and thioglycolate, pretreatment with acids has no effect on the load extension curve (Fig. 8). Acid buffers do not modify the load extension curves of unbleached, thioglycolate-treated hairs.

Discussion

The main result of our studies is the finding that *when hair is bleached with hydrogen peroxide, the ensuing damage does not cease when the bleaching process is ended.* In the course of bleaching, the hair becomes vulnerable to exposure to water and neutral aqueous solvents. The conditions under which water may extract certain components from bleached hair may be duplicated during the regular washing of the hair. Thus *every washing will inflict further damage*

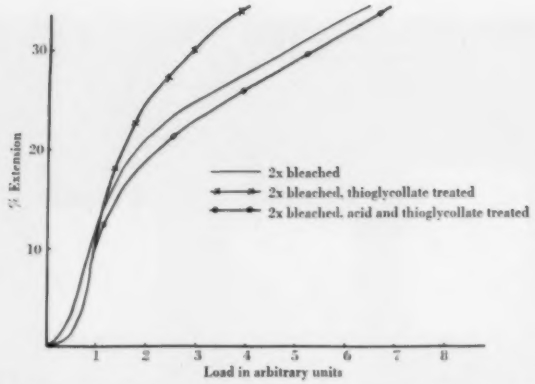

Figure 7—Acid treatment of bleached hair, prior to incubation with thioglycolate, often prevents additional damage caused by thioglycolate.

to the bleached hair, unless the hair has been pretreated with an acid solution of pH 2.0-3.8. The protective effect of a single acid treatment is probably sufficient to prevent further injury to the hair from one bleaching to the next, provided that the hair is being washed twice weekly for no longer than 30 minutes and that consecutive bleachings are spaced within 3 months. It is of interest to point out that the time-honored habit of rinsing the scalp with vinegar or lemon juice after washing, has a scientific justification in the case of bleached hair. The acidity of these rinses is in the effective pH range.

In practical tests, acid shampoos of pH 3.6 or less gave cosmetically excellent results, when used to wash out the excess peroxide and ammonia immediately after the bleaching process. One unavoidable drawback of these shampoos is the stinging pain experienced by the subjects whenever there is a slight wound or abrasion on the scalp. Many of the subjects commented on the improved appearance of the hair after such treatments, opinions which cannot be evaluated objectively.

From a more general point of view, the possibility was considered that these findings were applicable to other agents which acted through peroxide formation (X-ray, ultraviolet light) and to other keratinous structures. Irradiation of wool with ultraviolet light leads to the formation of sulfuric acid within the wool fibers; as a result, the fibers become more water-soluble (18). This situation is analogous to the behavior of hair treated with peroxide. However, the amount

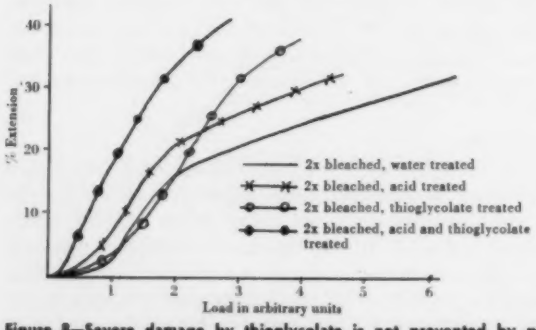

Figure 8—Severe damage by thioglycolate is not prevented by prior acid treatment; neither is damage caused by peroxide, as indicated by parallel courses of load extension curves.

of ultraviolet irradiation needed to produce this effect, far exceeds the physiological dose. In our own studies powdered epidermal keratin (callus) showed none of these effects when irradiated with ultraviolet light. This discrepancy may be explained by the relatively low sulfur content of epidermal keratin and the small amounts of peroxide produced. Although it would be attractive to postulate that acid sweat has the function of "solidifying" the surface keratin which has been damaged by ultraviolet light, at present this theory has no basis whatsoever. Nevertheless our studies again emphasize the known fact that the fate of keratin is not ended with its formation; it may undergo further profound chemical changes after the process of keratinization has been completed.

Summary

When hair, bleached with hydrogen peroxide, is exposed to water, certain decomposition products and oxidized pigment are extracted from the hair shaft. These conditions arise in everyday life during the regular washing of bleached hair.

Treatment of bleached hair, immediately after bleaching, with acid solutions of pH 2.0-3.8, greatly decreases its vulnerability to water. During the process of bleaching, acid groups are formed from the disulfide linkages of hair and some of its components become water-soluble. Acid pretreatment of the bleached hair apparently causes precipitation of water-soluble components within the hair shaft and thus makes the hair more resistant against subsequent damage.

The "hardening" of the acid-treated bleached hair is also manifested in its decreased sulfhydryl content and its greater resistance to damage caused by thioglycolates, as shown by load extension studies.

These findings indicate that when hair is bleached with hydrogen peroxide, the resulting damage does not cease when the bleaching process is ended, but recurs with every washing of the hair. A single acid treatment offers long-lasting protection against the repeated damage.

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Fred C. Theile speaks on the evaluation of Bergamot Oil

E. R. van Liew treats the male acceptance to use of fragrance

American Society of Perfumers Hold Sixth Annual Symposium

Highlighted by the award of honorary membership to Edward S. Maurer, the meeting was well attended by perfumers, executives, and guests from the cosmetic industry.

A large and appreciative audience of top names in the industry, assembled at the Essex House in New York on April 28th, paid a justly deserved tribute to Edward S. Maurer as president Bernard Polak presented him with an honorary membership in The American Society of Perfumers. Mr. Maurer is Senior Perfumer and Cosmetic Chemist, Lautier Fils Ltd., London; Member, U. K. Consultative Committee on Essential Oils; Member, Society of Cosmetic Chemists of Great Britain; Fellow of the Chemical Society; Fellow of the Royal Horticultural Society. He is also known for his book PERFUMES AND THEIR PRODUCTION published in England.

Various aspects of perfumery were well covered by a carefully selected panel of experts who presented their papers before the group. The following are abstracts of the papers.

A Modern Approach To The Evaluation Of Bergamot Oil, By Fred C. Theile, Donalr Dean and Robert Suffis, Shulton, Inc.

Bergamot Oil is one of the most indispensable essential oils on the perfumer's shelf, due to its well known superb odor. Appraisal of the oil from olfactory as well as chemical standpoints is extremely important.

Modern analytical methods are used to contribute additional data for more complete evaluations of Bergamot Oil.

Ultra Violet, Infra Red Spectrophotometric and Vapor Phase Chromotographic techniques have been employed to provide accurate and rapid means for detecting and identifying additions to natural Bergamot Oil. These have eliminated to a great degree tedious and complicated wet chemical methods of analysis and have provided means of determining per-

Officers of The American Society of Perfumers

Front: chairman Dr. Oliver L. Marton of Shulton, 2nd vice president Herbert Sommer of Prince Matchabelli, secretary Dorothy A. Douglas of Shulton, president Bernard Polak of Polak Frutal Works. Rear: director John Hancock of Warner-Lambert, treasurer Edwin D. Morgan of Lever Bros., directors Elmer L. V. Sulik and Edward J. Shuster of International Flavors & Fragrances.

Honorary Membership

President of The American Society of Perfumers Bernard Polak represents the scroll to Edward S. Maurer of Lautier Fils Ltd., London, England.

Alfred H. Moeller on human temperament and odor selection

Dr. Oliver L. Marton points to pitfalls in perfumery

Thomas Cifelli warns of patent problems in perfumery

Walter Lengsfelder traces the abstract concepts in perfumery

centages of natural Bergamot Oil in certain mixtures.

Analytical examples are shown where Bergamot Oils passed the N. F. tests but were found to contain either components out of proportion or materials not naturally occurring in Bergamot Oil.

The correlation and interpretation of analytical data obtained by the use of modern instrumental methods as presented, provides the perfumer and purchasing agent with supplemental information to aid in judging the qualities of variously priced Bergamot Oils.

Fragrance And The American Male, By E. R. van Liew, Givaudan-Delawanna, Inc.

The large yearly expenditure on men's luxury fragrance items and on shaving essentials by the American public is cited and analyzed. The cultural background of the modern American male is discussed in terms of his attitude toward fragrance. The author shows that modern man's jealous grasp on the concept of masculine dominance is his reaction to woman's many inroads into his "male domain of all but the major professions".

Some interesting paradoxes in the male's attitude toward toiletries are cited. Evidence is given which suggests that man is slowly beginning to accept fragrance at least as a part of functional products. The question of men's odors and women's odors is brought up with the conclusion reached that these differ from each other by very narrow, but nonetheless subtle and important margins.

The reader is cautioned that it is premature to make the American male aware that he has been accepting his favorite fragrances as "masculine" through the mediums of package design, product name and subconscious association with the functionality of the cosmetics he uses in his daily life.

The Influence Of Human Temperament In Odor Selection, By Alfred H. Moeller, Noville Essential Oil Company, Inc.

Consumer testing of fragrances sometimes proceeds under the assumption that people's tastes are wholly acquired and that deep seated instinctive reactions play no part in influencing the outcome of a test.

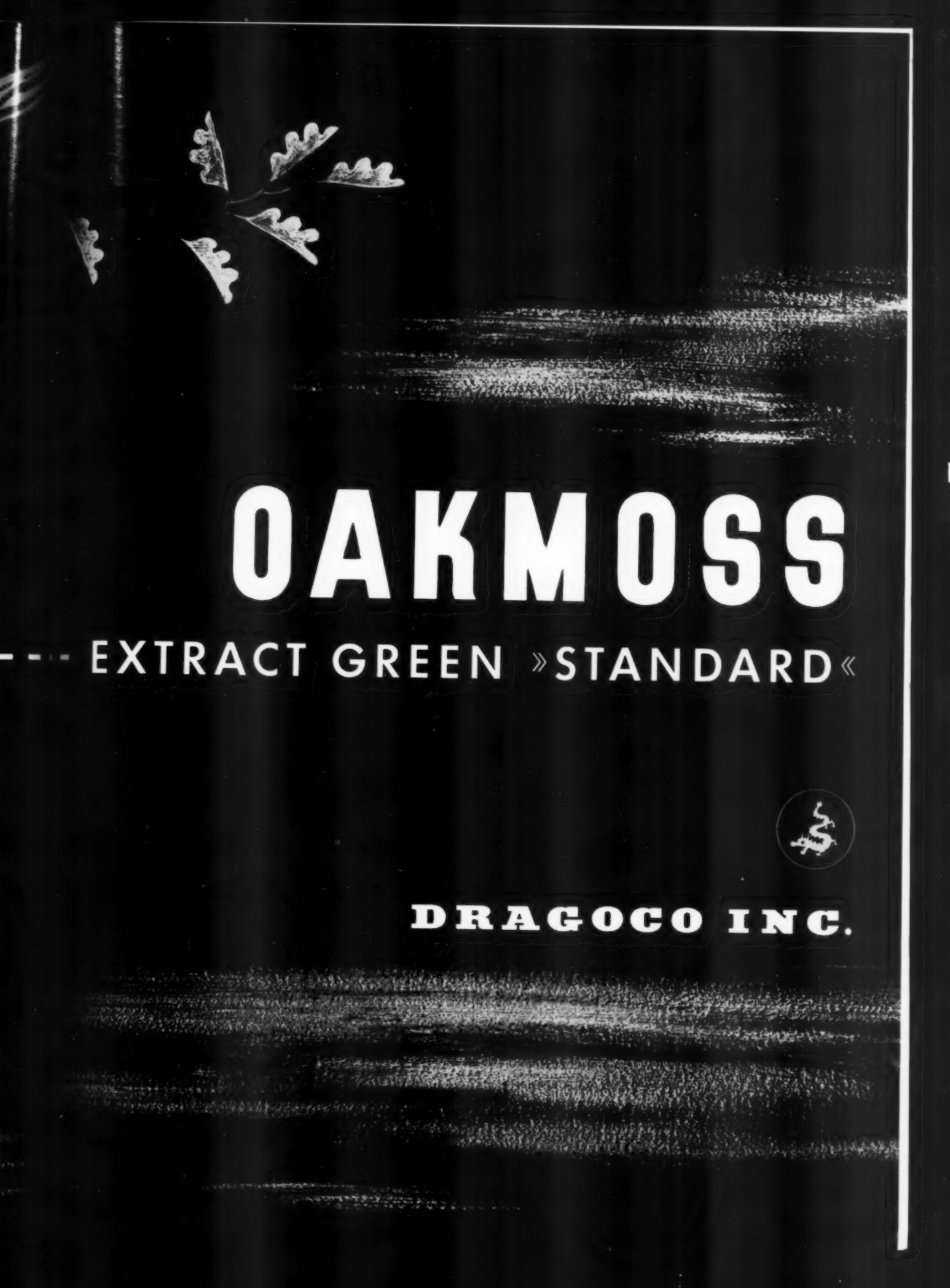
The question is raised, therefore, whether consumer tests can be fully relied upon when testers are picked at random from a segment of the buying public. Panel tests indicated that olfactory acuity is far from universal and that people who show a genuine interest in fragrances are in the minority.

The position is taken that we are partially influenced by deep seated instinctive likes and dislikes with regard to odors. It, therefore, is claimed that, (a) an individual does not select odors soley in accordance with his own acquired taste, (b) differences of taste between individuals are brought about not only by environmental influence.

An analysis of temperament in terms of three primary components suggests a way by which we can spot people who have the capacity to judge odors. Constitutional psychology, as systematized by William

Speakers and presiding officers: Walter Lengsfelder, symposium chairman, speaker E. R. van Liew of Givaudan-Delawanna, Inc., Edward S. Maurer of London and receiver of Honorary Membership, Dr. Oliver L. Marton, chairman of the Society, speaker Alfred H. Moeller of Noville Essential Oil Co., Bernard Polak, president of the Society, speaker Fred C. Theile of Shulton and discussion moderator Frazer V. Sinclair of Drug & Cosmetic Industry.

Curtain call is answered by Kay Colton, Morningstar-Paisley, Inc., Miriam Gibson French, McCall's magazine, Fannie Golstein, International Flavors & Fragrances, Inc., and Mary Hartwick, American Medical Association.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H. Sheldon forms the core of this investigation. The varieties of temperament according to the Sheldon theory are correlated to the varieties of human physique. Temperament, like human physique, is made up of three primary components. Relative strength of the primary components varies from person to person; this is recognizable through corresponding temperamental traits. Evaluation of these traits along lines of Sheldon's trichotomy gives not only an insight into people's temperamental make-up but also could help us select the kind of people who are temperamentally predisposed to provide meaningful answers to the problem of odor selection.

Pitfalls In Perfumery, By Dr. Oliver L. Marton, Shulton, Inc.

Pitfalls threaten from the very first moment a perfumer goes to work on a new fragrance composition. In fact, they occur at any stage of the perfume's lifespan, from the birth of the raw materials to the final evaporation of the fragrance at the time of application by the consumer. Every step of the perfumer's work, in addition to being creative, is governed by attempts —and sometimes even futile efforts—to avoid future pitfalls, right in the development stage.

Generally speaking, pitfalls in perfumery can be classified as belonging to one of three categories. They are caused by

1.) Lack of knowledge of (or in) perfumery
2.) Human negligence or inaccuracy
3.) The effect of unknown factors

Paul Johnson of P. Robertet & Cie, France, chats with John Hancock of Warner-Lambert Products.

Leonard Stoller and Pierre Bouillette of Givaudan-Delawanna, Inc. pair up with Maurice Meunier, vice president of Les Parfums De Dana, Inc. and Morris Jacobson of the same organization.

In detail, the speaker will show that pitfalls commonly encountered in perfumery are partly due to nature's trickiness and partly due to human shortcomings. Among the *natural* causes are sensitivity to light, heat and air of most perfume materials, the greatly varying physico-chemical conditions in the various toiletries and cosmetic items as well as in the packaging materials, the mathematical background of changes in perfume concentrations, and others. *Human* shortcomings responsible for pitfalls in perfumery express themselves in the delegation of perfumery decisions to non-perfumers, in wrong interpretation of literature references or of results, in wishful thinking governing the testing of fragrances under distorted conditions, to name the most frequent ones.

Examples are given elaborating the above. Some widely used producers are criticized as deviating from actual conditions, thereby unnecessarily encouraging pitfalls in perfumery.

Perfumers And Patents, By Thomas Cifelli, Jr., Richards and Cifelli, Patent Lawyers

The typical U. S. perfumer can continue to disregard patents in the future only at the risk of reducing the amount of his employer's profits and of increasing the chances of his empoyer being liable for patent infringement.

Main areas where perfumers can improve the profits picture will be discussed. These areas include new chemicals employed in perfumes, as well as new

American Perfumer's John H. Muller greets Edward J. Strobl, president of Albert Verley & Company.

Caught in the middle is Charabot's Edgar R. Ellis, flanked by Gert Keller and Bernard Wising of Schimmel & Co., Inc.

functional or ornamental containers for perfume products.

It will also be shown that the recent widescale extension of the U. S. perfumer's work into field of "industrial" products has brought a much greater risk of patent infringement than was the case when the perfumer was chiefly interested in creations for Milady.

Some practical suggestions to aid the perfumer in meeting his added responsibilities will be offered.

The Abstract Concept In Perfumery, By Walter Lengsfelder, Fleuroma, Inc.

As far back as we can trace mankind, there has been art and as far back as we can trace art, there has been abstract thinking. In fact, any thinking must be abstract in order to be artistic.

If we understand certain elements in the evolution of painting, we can then draw a parallel for Perfumery. This parallel will clarify and make us aware of where we perfumers stand today and will prepare us for the task of creating the exciting fragrances of the future.

With the help of color slides, it is shown how the abstract concept of painting has developed since Deguerre and Niepce published the invention of photography, and afterwards—parallel to this—how Perfumery has developed since Friedrich Woehler synthesized the first Organic Chemical.

From descriptive floral perfumes to the modern perfume creations there is a definite development towards the abstract.

The abstract concept in Perfumery will be demonstrated by a new aromatic which will be shown to the audience. It will illustrate the prerequisites for this abstract concept as discussed by the Speaker.

The Speaker will point out that the final odor of a perfume describes means little as long as the beauty of the fragrance is maintained.

One of the conclusions that will become apparent is that Perfumers do not have to be afraid to deviate from Nature's fragrances because, no matter how abstract their endeavors, their achievement will still be earthbound. In the final analysis, any creative person by virtue of being human, can only create within the vast framework of Nature itself.

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A Comparison of Hair and Textile Coloring

By Dr. H. Wilmsmann
Ondal, G.M.B.H., Development Laboratories

Textile dyestuffs are considered as possible human hair coloring agents in this paper. The dyes to be discussed are classified in Tables 1 and 2.

Table 1

Classification of the Textile Dyestuffs from the Chemical Standpoint

Nitro-dyes	
Nitroso-dyes	
Diarylmethane-dyes	
Triarylmethane-dyes	Malachigreen-, Fuchsin-, Aurin-, Phthalin-, Acridine group
Azine-dyes	Phenazine-, Oxazine-, Thiazine group
Anthraquinone-dyes	
Indigoid-dyes	Indigo-, Thioindigo group
Vat-acid-esters (solubilized vat dyes)	Mono-, Di- and Polyazo, metal-complex- and azo dyes
Sulfur-dyes	
Azo-dyes	water-insoluble and by sulfo groups or quaternized groups
Phthalocyanine-dyes	water soluble phthalocyanines, also phthalocyanines formed in the fiber
Methine and Azomethine	
Oxidation dyes	

Table 2

Classification of the Textile Dyestuffs from the Color Standpoint

Acid dyes
Mordant dyes
Direct dyes
Basic dyes
Sulfur dyes
Vat dyes
Solubilized Vat dyes
Azo dyes
Oxidation dyes

The dyeing of textiles or hair with these dyestuffs is possible only by first penetrating into the fiber by *diffusion* and then by fixation in the fiber. Textile

This is a translation by the author based on an article appearing in *Parf. u. Kosm.*, 40 443 (1959) as presented before the German Society of Cosmetic Chemists June 6, 1959 at Heidelberg.

and hair coloring are therefore discussed from the following consideration with regard to *diffusion* and fixation.

Dyeing of Textiles

A. The Diffusion of the Dyestuffs into the Fiber

The diffusion of the dyestuffs from the dye solution into the fiber begins with the diffusion from the solution into the contacting surface solution fiber, followed by diffusion from this border-layer into the fiber.

I. Diffusion from the Solution into the Border-Layer

According to Fick's laws, the number of moles **dn**, which passes the area **q** in the time **dt** at the concentration-difference **dc/dx**, is given by the equation

$$\frac{dn}{dt} = -D\,q\,\frac{dc}{dx},$$

the diffusion-coefficient **D** being a factor of proportionality, that defines the number of moles of the diffusing substance passing the area of 1 cm^2 in a certain solvent at a given temperature in the time-unit and at the concentration-difference of 1. The diffusion-coefficient raises with the temperature and lowers with increasing particle radius of the diffusing substance and increasing viscosity of the dye solution.

The diffusion from the solution into the border-layer can therefore be accelerated by means of raising temperature and concentration-difference and diminution of the size of dyestuff-molecules as well as viscosity of the dye solution.

II. Diffusion from the Contact Surface into the Fiber

1. The influence of the electro-kinetic potential (zeta potential). Between the fiber and the contact surface, there is an electro-kinetic potential able to accelerate or to check the diffusion of the dye particles according to their electric charge. Neale and Peters (3) and Stackelberg, Kling, Benzel and Wilke (4) have measured these potentials as follows:

Table 3

Fiber	Neale, Peters (mV)	V. Stackelberg et. al. (mV)
Vinyon	−46	..
Orlon	−44	..
Terylene (Dacron)	−32	..
Wool	−31	−62
Cellulose acetate	−28	−58
Polyvinyl chloride	..	−48
Silk	..	−42
Nylon	−22	..
Perlon	..	−39
Cotton	−17	−32
Viscose rayon	..	−32

The potentials in both reports are not identical due to different methods of measurement, but the succession is the same.

These potentials show that the diffusion of cationic dyestuffs, i.e., of the positively charged ions, is generally favored, whereas anionic dyestuffs must have an electric potential less negative than the potential of nomionic fiber polyacrylonitrile with acid dyes due the fiber. This can be achieved by the addition of nonionic fiber polyacrylonitrile with acid dyes, due certain acidic salts, producing with wool a cationic effect, below the isoelectric point.

The nonionizable fibers may not be altered by pH variation, of course. So it is impossible to dye the to the dense packing of its chain molecules but especially to the high negative electric potential. This fiber can be dyed with acid dyes by means of the so-called "cupro-ion-procedure." To the dyeing solution there are added cupro ions which can approach and penetrate the fiber by their positive charge and form stable, positively charged complexes with the nitrile groups. Hence a loosening of the fiber structure as well as a shifting of the potential to positive values takes place, the dye anions now being able to approach and penetrate the fiber and to form stable salt bondings with the copper nitrile complexes.

2. The influence of thermal movement (Brownian movement of molecules).

Park (5) found in his investigations about the diffusion of halogenated hydrocarbons into polystyrol, that the diffusion coefficient depends on the mol-volume (V) of the diffusing substance and the diameter of the smallest spaces (d) of the fiber:

$$D\,k\,e^{-\frac{V - Bd}{}}$$

This equation is in its principle valid for the diffusion of dyestuffs from the border-layer into the fiber, too. The diffusion coefficient becomes lower, the larger the dye molecules and the smaller the intermicellular spaces in the fiber.

The diffusion coefficient also depends on the dyeing temperature. The increase of dyeing velocity by raising the temperature is explained by Vickerstaff (6) as follows:

By the increase of the thermal movement of the chain molecules in the fiber, there is a greater probability for the approaching dye molecule to find a space for penetrating it. The probability to find a space is relatively little influenced by temperature using fibers with a loose structure. In the case of a fiber structure of a high degree of arrangement, with many bridge bondings, the probability of "hole-formation" is closely connected with the amplitude of the thermal vibration, i.e., such structures react very sensibly upon raising the temperature in their dyeing velocity.

The degree of arrangement and hence the dependence of dyeing velocity on the temperature may be measured by the activation energy. According to the statements of Vickerstaff (6) when dyeing this energy is:

wool with milling dyestuffs	29 kcal/Mol
nylon with disperse dyes	22 kcal/Mol
cellulose acetate with disperse dyes	20-24 kcal/Mol
cellulose with direct dyes	12-14 kcal/Mol
terylene (dyestuffs not mentioned)	30 kcal/Mol

The exhaustion of the dyeing solution by the different fibers depends on the dyeing temperature according to their activation energies as follows:

Table 4

kcal/Mol	60°	80°	100°	125°	150°	200° (C)
15	10 h.	2.5 h.	1 h.	15 min.	6 min.	45 sec.
20	1 day	4 h.	1 h.	11 min.	2.5 min.	12 sec.
25	2.5 days	7 h.	1 h.	7 min.	1 min.	3 sec.
30	5 days	12.5 h.	1 h.	5 min.	0.5 min.	1 sec.

As wool has an activation energy of 29 kcal/Mol (the dyeing time of the bottom row of Table 4), one can understand that dyeing of wool may be more influenced by raising temperature than dyeing of cotton (dyeing time of the top row of Table 4).

From these results, the diffusion of dyestuffs into the fiber is favored by

1. raising of temperature
2. increase of dye concentration in solution
3. swelling of the fiber
4. diminution in size of dye molecules
5. adaption of the electric potential of the fiber to the state of electrical charge of the dye ions
6. diminution of viscosity of dyeing solution

B. Dyeing of Cotton with Direct Dyes

Cotton consists of cellulose fibers with chain molecules of about 500 cellobiose units. These chain molecules are partly in a crystalline, partly in an amorphous state. When cotton is brought into a dyeing solution of 100°C., at first the water penetrates the amorphous parts forming openings with a diameter from 50 to 100 A°. Dye molecules with a extension of more than 100 A° are not suitable for dyeing of cotton. The dyestuff molecules form aggregates of a few molecules in the solution which are in equilibrium with the singular molecules, only the latter generally being able to penetrate. The singular dye anions of direct azo dyes have a length of about 20 to 30 A° and may therefore penetrate. These dyes are fixed in the fiber by Van der Waals forces and hydrogen bonds, the latter being of decisive importance. The dyestuff must fulfill certain steric conditions enabling them to form a number of hydrogen bonds sufficient for good fixing. The partners of the hydrogen bonds are on the cellulose side OH groups; on the dyestuff side OH-, NH_2-, and carboxamide groups One cellobiose unit takes about 10, 3 A°, that means the distance of equivalent OH groups is 10, 3 A°. Therefore, the dye molecules must also have a length of 10, 3 A° between those groups participating in hydrogen bonding. This distance will be found among the dyestuffs of the benzidine type, azo dyes with 6-amino-1-naphthol-3-sulfonic acid (J acid) and a few other types, so that the class of direct cotton dyes consists preferably of these types.

II. Dyeing of Cellulose Acetate with Disperse Dyes

The arrangement of the cellulose molecules is similar to that of cotton, but the number and volume of the spaces between the micelles is diminished, caused by acetylation and spinning process, thereby decreasing the ability to swell. Besides that, the possibilities to form hydrogen bonds are lessened due to the reduced number of free OH groups.

The disperse dyes are acetone and ester soluble dyes of the azo and anthraqinone type. It is assumed that the dyes are dissolved by the acetate fiber out of the dispersion in water due to its lipophilic character; the fixing of the water insoluble dyes being accomplished by forming a true solution. As it is impossible to decolorize the dyed acetate fiber by excessive acetone, it is supposed that also some hydrogen bonds are formed with residual free OH groups.

III. Dyeing of Wool with Acid Dyes

The wool fiber is also composed of crystalline and amorphous parts consisting of polypeptide chains with cystine bridges. In this texture of crystalline and amorphous areas there are openings reaching a diameter of about 35 to 40 A° formed by absorbing water from the dye solution at 100°C. Dyestuffs with a molecular size corresponding to these measurements may penetrate and are fixed by Van der Waals forces, salt and hydrogen bonds. In the case of metal complex dyes there is an additional possibility of fixing by coordinate bonds between the metal atom and hydroxyl amino groups of the wool.

IV. Dyeing with Vat Dyes

The sodium salts of the leuco compounds penetrating the fiber are fixed by hydrogen and Van der Waals bonds. When the excessive, unbound parts are removed by washing, the bound parts are transferred to water insoluble and therefore well anchored products by means of oxidation. These final products have no more affinity to the fiber, but they are well fixed in the fiber spaces due to their insolubility in water.

V. Dyeing with Azo Dyes

Cotton is first treated with a naphthol of the AS series which must have a substantivity to the fiber similar to the direct dyes. After the removal of the excessive naphthol, the azo dye is developed by coupling in the fiber with a diazonium salt. The formed azo dyes are not water soluble and therefore well fixed within the fiber. Many dyestuffs with the well-known "indanthrene" fastness properties belong to this class.

VI. Dyeing with Basic Dyes

1. Wool

Due to their basic character these dyes are capable of forming salt linkages.

2. Cotton

Basic dyes have practically no substantivity for cotton. If cotton is pretreated with tannin, which is substantive to cotton itself, dyeing of cotton with basic dyes is possible by forming salt linkages with the acid groups of the tannin.

VII. Dyeing with Mordant Dyes

The fiber is pretreated with metal salts, such as aluminium or chromium salts. With wool, the salts form metal protein complexes. Cotton must first be treated with rancid olive oil ("old red proceeding") or with turkey red oil ("new red proceeding") in order to get substantivity of the metal salts, the insoluble metal soaps being formed in the fiber. Now the fibers are treated with dyestuffs which are capable to complex formation according to their chemical constitution, such as alizarine. There is a dye lak formed in the fiber, and it is well fixed by its insolubility in water.

VIII. Dyeing with Aniline Black

Aniline black is produced in the fiber by oxidation of aniline hydrochloride or p-amino-diphenylamine. These amines are substantive, giving salt and hydro-

gen bonds. After oxidation they are insoluble in water and therefore firmly anchored in the fiber.

IX. Dyeing with Reactant Dyes

1. Procion and Cibacron dyes (ICI and CIBA)

The Procion dyes consist of cyanuric chloride connected to one dye molecule, the Cibacron dyes of cyanuric chloride connected to two dye molecules, the first type having two atoms of chlorine free for reaction, the latter, one atom of chlorine. Cotton as well as wool is dyed with these dyestuffs, true chemical (homoopolaric) bonds being formed with splitting off of HCl.

2. Remazol Dyes (Hochst)

At first sulfuric acid is split off from these dyestuffs in the dye bath with formation of dye vinyl sulfones. The unsaturated vinylsulfones add to reactive groups of wool or cotton and also form true chemical bonds between dyestuff and fiber.

The reactant dyes solve the problem of fixing in an ideal manner. The fastness properties against wetting, washing and rubbing are therefore excellent.

X. Textile Printing with Pigments

Organic and sometimes inorganic pigments without any affinity for the fiber are fixed on the fiber surface by means of binders. A satisfactory solution to this problem was found in synthetic resins that can be hardened by heat. A dispersion of pigments and resin is printed on the fiber and fixed by a short heat treatment at 120 to 130°C. True chemical bonds are produced between the fiber and the resin binder. The fixing of the pigments is hence accomplished by embedding them into a film firmly fastened to the fiber surface.

According to these considerations, there exist the following possibilities for the fixing of dyes:

1. Forming of salt, hydrogen and Van der Waals bonds between dyestuff and fiber. If hydrogen bonds are the only linkage, steric moments are of special importance, meaning that structure and size of the inter-micellular spaces must correspond to the structure and size of the dyestuff molecule, including the distance between reactive groups of fiber and dyestuff.

2. Fixing of water insoluble dyes is possible by true solution in the fiber.

3. The dyestuffs from true chemical bonds with the fiber.

4. Fixing of dyestuffs or pigments may be accomplished by embedding them into a resin film on the fiber surface, the resin film being firmly attached to the fiber by true chemical bonds.

C. Fastness Properties of Textile dyeings

The value of dyeing depends on the achieved shade, its fastness properties and on economic considerations. The fastness properties depend on the kind of dyestuff and fiber, the amount of absorbed dyes and the dyeing procedure. Of special importance is the wear fastness against the influence of weather, light, washing, ironing, sea water, sweat, rubbing and alkali.

Dyeing of Human Hair

The results of the considerations of textile dyeing will now be applied to dyeing human hair.

A. Diffusion of Dyestuffs into the Hair

I. The Influence of Temperature

The size of the intermicellular spaces of a fiber and the degree of arrangement of its chain molecules are decisive for temperature dependence of diffusion. It may be assumed that the degree of arrangement of the keratine fiber hair is similar to that of the keratine fiber wool, so that hair dyeing also will respond very sensibly to variation of temperature. For physiological reasons hair dyeing can be carried out at maximum temperatures of 45 to 50°C. Therefore, the influence of the thermal vibration of the molecular chain and hence the probability of an approaching dye molecule to find such a space is small. For this reason, most of the dyestuffs suitable for dyeing wool cannot be used for dyeing hair due to their molecular size. The dyeing of hair is therefore to a special degree restricted to the use of dyestuffs consisting of small molecules, as raising the temperature up to 50°C., can produce only a slight effect.

The industry offers nowadays so-called "hair saunas" (steamers), which produce a moist, warm atmosphere of up to 50°C. Their application reduces the dyeing time, (which lasts about twenty to thirty minutes at room temperature) to about a half.

II. The Influence of Dye Concentration

The dye concentration may be varied within the range of solubility, but there exist certain restrictions. The achievement of level dyeing is favored by choosing the dye concentration as high as possible for the desired shade, and diminution of dye substantivity by the addition of effective leveling agents having affinity either for the fiber or the dyestuff. Hair dyes of high viscosity containing certain leveling agents, such as cream hair dyes, are in spite of higher dye concentrations, superior to liquid hair dyes with lower dye concentrations with regard to level dyeing.

III. The Influence of Fiber Swelling

As swelling cannot be achieved by raising temperature over 50°C., it is of special importance to perform swelling by chemical means. The isoelectric point of hair being at about pH 4.7 to 4.9, differing pH values bring some swelling effects, the swelling within the physiological limits being much stronger in alkaline medium. Ammonia is preferably used as an alkaline swelling agent.

Many other swelling agents have been proposed, but most of them have been shown to have no use. Such agents often swell and dye the skin too, or they are toxic, or produce undesired dyeing results.

Permanent waved, bleached and "damaged" hair swells more with water than native hair and brings about generally more intensive dyeing (8, 9). Similar results, but to a lesser extent are obtained with hair pre-dyed parts easily are more intensively colored than the undyed regrowth. This difficulty can be overcome by the formula of the hair dye as well as by the right dyeing technique.

IV. The Influence of the Molecular Size

As substantial swelling of human hair, compared with wool swelling, cannot be achieved by raising the temperature or by chemical means known up to this day, the size of the dye molecule is of decisive importance. Besides this one must remember that also the diffusion of the dyestuffs from the dye bath

(e. g., from a cream hair dye, into the interfacial layer bath/fiber) depends on the molecular size. Whereas in dyeing of textiles diffusion can be aided through mechanical moving, such a mechanical aid in dyeing hair is only possible by combing from time to time, thereby having only a slight effect.

If penetration of the dyestuffs into the inner parts of the hair shaft shall be achieved (important for good light fastness), and not only a superficial absorption, the molecular size of the dye must not exceed that of naphthalene or anthracene. Dyestuffs with more nuclei, e. g., basic triphenylmethane dyes, generally produce in the new growth only superficial, peripheral dyeing, whereas they penetrate deeper into the hair ends or bleached hair.

As about 80 per cent of all hair dyes are made in brown and blonde shades and just the brown dyestuffs have a relatively large molecule, it may be understood that the common textile dyes, alone for this reason, are of less importance in hair dyeing. On the other hand is the necessary restriction in molecular size an essential supposition for the eminent importance of the oxidation dyes in dyeing of human hair, because these starting compounds having small molecules are able to penetrate the hair and form the large sized color molecules in the intermicellular spaces by oxidation after having penetrated.

Besides the oxidation dyes only the nitro dyes are of importance in hair dyeing. They are nitroaminobenezenes, nitroaminophenols and their alkyl derivatives, all possessing small molecular size. With these nitro dyes, yellow, orange, red and violet shades may be achieved.

V. The Influence of the Electric Potential

Hair has, like wool, a strong negative electric potential. It is therefore difficult to dye human hair with anionic dyes. If the hair is prewashed with a cationic shampoo, considerable absorption may be attained with acid dyes, because the negative charge of the fiber is diminished (11). Such dyes have only poor fastness against rubbing and washing, this process therefore being of interest only for so-called "theatrical dyes," which are intended to be changed often.

The negative potential of hair favors the diffusion of basic dyes.

VI. Relations between Dyestuffs and Human Skin

Contact of the dyes with the hands can be avoided by a suitable dyeing technique. However, considerable contact of the dyes with the skin of the head occurs quite naturally, because the treatment of undyed new growth near the skin is essential.

Dyestuffs dyeing only the hair but not the skin are not known, but there are significant differences between the several classes of dyes. While oxidation dyes stain the skin very much less than the hair, basic dyes behave oppositely. Certain acid dyes dye hair well, but small, ring-like stains of the skin around the follicles may be seen.

Such dyestuffs cannot be of any practical importance.

To prevent running down of the dye, cream or gel preparations are in use, also liquid dyes which thicken when mixed with hydrogen peroxide just before use. It requires some experience to develop a hair dye composition of the right viscosity which does not run, yet enables the dye molecules to penetrate the diverse additional demands not being mentioned.

The behavior of hair dye compositions is of special importance for physiological reasons (12). The index of allergy caused by a cream hair dye is stated to be in the range of 0.0001 to 0.0002 per cent (referred to sold units). This amazing result supports the opinion that it is possible to prevent the penetration of the dyes into the skin by certain emulsion systems.

VII. The Coloristic Behavior of Different Hair Structures

While textiles have generally uniform structures (with the exception of mixed fibers whose differences are regular) the differences in the structure of human hair are very great. Level hair dyeing is therefore an essential problem. The regrowth of the hair, about 1 cm. per month, has to be dyed about once a month, the already dyed parts must not show any dye addition by overlapping.

The variability of hair structures comprises regrowth, middle and top parts of the hair, cosmetic pretreatments, influence of light (say at the sea or the mountains) and racial differences (9). All these different structures imply principle different diffusion velocities, e.g., it is very difficult to get a brown shade by combination of blue, red, yellow, as these dyes in spite of similar substantivities fractionate in some cases. Thus the regrowth may be dyed red and the hair tops green.

Though the difficulties for the achievement of good leveling are considerable, this problem has been solved satisfactorily by modern hair dyes.

VIII. The Dyeing Time

Good leveling is favored by reducing the dyeing velocity. In textile dyeing there are dyeing times of several hours. Dyeing of human hair requires much shorter periods for economic and practical reasons. Today a dyeing time of about fifteen to thirty minutes is common. Together with the other treatments such as washing, perhaps permanent waving, hair cutting, fingerwaving and drying a total time of several hours may elapse for both client and hairdresser.

B. The Fixing of the Dyes in the Hair

The possibilities for fixing (existing in textile dyeing) seem to be applicable for hair dyeing, too.

I. Fixing by Forming of Salt and Hydrogen Bonds

Hair as wool being of amphoteric nature, salt linkages may be formed with basic as well as with acid dyes. The already mentioned nitroamines and nitroaminophenols should be linked also through hydrogen bonds.

II. Fixing of Water Insoluble Dyes by True Solution in the Hair Keratin

This principle, known from dyeing cellulose acetate with disperse dyes, is scarcely realized in hair dyeing, though under suitable conditions disperse dyes exhibit a certain substantivity for hair. It might be imagined that these dyes could be dissolved by the hair lipoids; but the existance of these as constitutional

ingredients of the hair keratin has not been proved. So it must be supposed that the slight substantivity of disperse dyes to hair is due to hydrogen bonds.

III. Fixing of Dyes by Transfering Water Soluble Starting Materials To Water Insoluble Dyes

The fixing of the important oxidation dyes follows a definite principle. The following compounds, the molecular size of which does not exceed that of naphthalene, are generally used:

(a) 2,5-diamino-toluene; 4-aminophenol; 4-amino-diphenylamine; 1,4-diaminobenzene (not allowed by law in some countries)

(b) resorcin, chloro-resorcin, 3-amino-phenol, 2,4-diamino-anisol, 2,4-diamino-toluene, a-naphthol

Whereas the compounds named under (a) react with alkaline H_2O_2 in the intermicellular spaces of the hair to higher molecular compounds of the phenazine or oxazine type, this does not occur with the substances named under (b) when used alone. The latter lead to oxidative dyeing only when used together with compounds of the (a) group. They serve to get certain shades and to improve the fastness properties. The oxidation products are well fixed because they have become water insoluble. It is not known whether there are other bonds between these oxidation products and the keratin. One can imagine that reactive groups of the keratin may take part in the oxidation process, forming true chemical bonds and perhaps other linkages, but this is only a theory not necessarily explaining the efficient fixation of the oxidation products.

The alkaline oxidation of the afore mentioned compounds with hydrogen peroxide leads to the following shades:

2,5-diaminotoluene	reddish brown
4-aminophenol	reddish blond
4-amino-diphenylamine	violet to black
2,5-diamino-toluene + resorcin	blond to brown
2,5-diamino-toluene + 3-aminophenol	blue grey
2,5-diamino-toluene + a-naphthol	violet blue
2,5-diamino-toluene + 2,4-diamino-anisol	blue
4-aminophenol + a-naphthol	wine-red

These dye precursors may be contained in a cream emulsion, alkalized with ammonia. The consumer mixes this product shortly before use with hydrogen peroxide and applies it to the hair.

The alkaline medium is necessary for two reasons:

1. to achieve swelling of the hair fiber
2. to achieve in combination with the H_2O_2 the oxidation of the dye intermediates and, most important, a certain bleaching effect.

The parallel occurring bleaching process shall prevent color addition at the already predyed parts of the hair. Besides that, it becomes possible to "dye the hair lighter," that means that the dyed hair is lighter than the natural shade of the hair before dyeing (13).

IV. Fixing of Dyes by True Chemical Bonds

1. Procion, Cibacron and Remazol Dyes

These dyes need higher dyeing temperatures than can be applied for physiological reasons. Besides that, they stain the skin badly.

2. Metallic Dyes (14)

Silver, copper, nickel, cobalt, bismuth, iron or lead salts in water solution are brought upon the hair. In the course of days to weeks, these salts react with the sulfur of the keratin to form colored metal sulfides. Since the dye develops so slowly, it brings about the illusion of a "natural process;" this class of hair dyes therefore have been sometimes called "hair color restorers." To accelerate this dyeing process, such reducing agents as pyrogallol, sulfides or thiosulfates may be added.

The metallic dyes have been used to achieve natural looking shades from blond to black, but for reasons of toxicity and application, their use has mostly been restricted. Lead, uranium, chromium, mercury, cadmium and tin salts are forbidden for cosmetic use in some countries. As all interesting metal salts catalyse the decomposition of hydrogen peroxide, a metallic dyed hair makes for great difficulties in all treatments using hydrogen peroxide, e.g., permanent waving (neutralization), bleaching or oxidative dyeing. Excessive heating of the hair, severe damage of the hair structure, discoloration or bad waving results are observed.

V. Fixing of Dyes by Embedding them in a Resin Binder on the Hair Surface

Pigment printing of textiles with sufficient fastness properties in deep shades is possible only if the dyes are embedded in a resin binder, which is firmly anchored to the fiber by true chemical bonds. Up to now there is no analogous process for use on human hair under physiological conditions.

Recently it became possible to develop such resin binders which are relatively firmly linked with the hair; wet and fast rubbing hair tints now being achievable. In this way hair may be gently toned without the necessity of after washing or rinsing. As the hairdresser is generally used to the application of fingerwave lotions as final treatment, one can achieve tinting and fingerwaving in a one way process.

Finally there are preparations, mainly of the aerosol spray type, which combine film producers such as shellac, polyvinylpyrolidone, ester resins, etc., with dyestuffs. As these 'binders" have only weak affinity to hair, the rubbing fastness of these colorants is unsatisfactory. Such preparations are therefore of interest only to achieve short-time fashionable effects.

C. Fastness Properties of Hair Dyes and Toners

I. Hair Dyeings

1. Light Fastness

The demand of sufficient light fastness is limited to four to six weeks, because the hair must be redyed after this time due to the regrowth. Whereas any change in shade must not occur, some lessening in the dye depth might be acceptable.

2. Fastness Against Cosmetic Treatments

Fastness against permanent waving is of special importance. The hair dye must be resistant to mercaptans (strong reduction) in alkaline or acid medium and to neutralization with H_2O_2 or bromate). Besides that, the dye must not be sensitive to pH variations between 3 and 10.

3. Fastness against Wetting, Washing, Sweat and Rubbing

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advertisement

SPEAKING FROM DENMARK

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SPEAKING FROM SWITZERLAND

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REVIEW OF Glycerine IN HAIR PREPARATIONS

SHAMPOOS, RINSES, LOTIONS AND TONICS, RECONDITIONERS, FIXATIVES AND LACQUERS, DRESSINGS

by Erik Thomsen

SHAMPOOS. It is always desirable that shampooing be accomplished in such a way that the resulting hair is not left in a condition of fluffiness, caused by lack of adherence or static electricity. As the demand of the buying public is still for a good foaming shampoo, it has—as far as I have seen—not yet been possible to create a shampoo to be sold completely without that downy fly-away hair drawback. In any event, glycerine is considered by some to be a helpful aid. Powers mentions, "Glycerol helps retain moisture and delay evaporation. Addition in shampoo formulations keeps the hair softer and helps moisture retention." For other reasons, I find glycerine of great value as a shampoo ingredient. It can act as an aid in manufacture, as a clarifier or a bodying agent. I have to admit, that my experience regarding soap shampoos is of little value, because we in Denmark have very hard water, rendering the soap type shampoo unsatisfactory and not very popular. For the manufacture of liquid soaps, however, I know how useful glycerine is. If it is not already present in the product as a result of saponification of fats, it simply may be added. Practically all formulas for soap shampoos in the literature contain glyc-

(Continued on Page 2)

HEAT-WAVING, DYEING, REMOVING AND STRAIGHTENING

by Dr. R. Heilingotter

HEAT-WAVING. The incorporation of "oily" substances into heat-waving lotions is considered beneficial to the hair. In order to minimize hair damage by the action of heat and the alkalinity of heat-waving lotions and to overcome hair dryness, these preparations are often provided with suitable additions of glycerine, especially to those which are applied at higher temperatures. According to Sarensen (1) an addition of half per cent glycerine, especially for difficult to handle, coarse hair, is suitable as a softening medium:

Sodium sulfite	10	parts
Ammonium carbonate	8	"
Ammonia 26%	2	"
Glycerine	0.5	"
Water, to make	100	"

Glycerine serves also to give a desirable lustre to the finish of the hair after it has been treated with the permanent-waving liquid. For the same reason Janistyn (2) suggests the following formula for a heat-waving lotion:

(Continued on Page 3)

erine, which illustrates the necessity of its presence as a clarifier (solubilizer), an antifreeze, a thickener, perhaps a foam stabilizer—as well as a hair conditioning agent.

What has been said above regarding soap shampoos is valid also for soapless shampoos; there will always be a reason for the addition of glycerine to a shampoo. I have in my own practice successfully used it as a bodying agent and an antifreeze in a liquid shampoo for hair-dressers, and in a cream shampoo based on Sodium laurylsulphate (in an amount of circa 5%) to prevent granulation of the cream during storage.

RINSES. In the days of soap shampoo, a hair rinse was simply a solution of a weak organic acid, used to dissolve the deposit of lime soap that would otherwise leave the hair dull and without lustre. Today a hair rinse is used to bring about better setting properties of the hair, to prevent fly-away after-shampoo effect, and eventually bring about brilliance to the hair. To promote that, a modern rinse will have to contain a cationic agent, a humectant and some oily substance. It may be presented to the customer as a one-use-pack or in larger bottles. It will appeal most to the buyer, if it has a creamy appearance, looking more "nourishing" than the plain clear solution. It may be provided with a suitable dyestuff, making a color rinse. Here is a simple emulsion to be used as a starting point for further development:

HAIR RINSE

Ethoxy lauryl ether	5	Glycerine	4
Heavy white oil	16	Ethanol 96%	16
Laurylpyridiniumchloride	0.2	Water	58
Polyvinylpyrrolidone	0.8	Perfume to suit	

The mixed oil and emulsifier are stirred during slow addition of the water. When the emulsion is finished, add the rest, and finally the alcohol.

LOTIONS AND TONICS. The same role is played by glycerine in alcoholic lotions in building a moist film around each hair shaft. Here partial dehydration is often brought about by the plain alcoholic solutions of perfume. A humectant helps eliminate this. The amount of glycerine in alcoholic hair lotions (if containing vegetable extracts or drugs generally called tonics) may vary from 2-12%, increasing with the water content. If kept at a reasonable ratio to the water (not over 1:4) in the lotion there is no risk of making a too heavy and slowly penetrating preparation. Glycerine will make the hair soft, supple and brilliant. In certain cases it even will help in keeping the perfume in solution and the lotion crystal clear.

HAIR RECONDITIONING CREAMS. The defatting action of the modern shampoos and the more and more frequent practice of dyeing and waving treatments with serious consequences to the hair and the scalp have resulted in a still increasing demand for preparations with the capacity of restoring the hair qualities lost during the mentioned proceedings, as for instance lustre, suppleness and softness.

Usually reconditioning creams contain lubricants (petrolatum, mineral oil, fatty esters, etc.), body giving substances (fatty alcohols, waxes, spermaceti), nutrients (lanolin, lecithin, hair hydrolysates, linoleic acid), emulsifiers, and humectants such as glycerine. The following formula for a hair reconditioning cream, which is very easy to make, simply by stirring the two phases together at a temperature of 70° C, perfume, cool and pack, gives a rather stiff cream, which the hairdresser must dilute with water to a semifluid emulsion before applying it to the hair after shampooing or permanent waving.

NOTE: Inclusion of formulations in this series of articles does not constitute a recommendation by G.P.A.—nor warrant that they are free from patent or other legal restrictions.

Cetostearyl alcohol	20	Sodium laurylethoxy-sulphate	1.5
Hydrogenated sperm oil	2	Glycerine	5
Soya lecithin, extra light	1	Boric acid	0.5
White oil	3	Polyvinylpyrrolidone	0.5
Isopropyl linoleate	2	Water to make	100

Perfume, colour, preservatives q.s.

As the cream is intended to be rinsed out of the hair after having been in the hair as a treatment for about 15 minutes, the glycerine content is here kept as low as 7% of the water phase. At that level it is believed to have a good chance of penetrating into the hair shaft, remaining there after rinsing and exercising a softening, swelling and humectant action in the hair. Using too high a content of glycerine will result in reduced penetration.

Besides this "treatment" property of glycerine, it also adds to the keeping properties of the cream—which, as it will be used in hair dressing salons, probably will be packed in jars, and consequently be prone to drying.

FIXATIVES AND LACQUERS. The purpose of these two types of non-greasy hair dressings is the same, the difference principally based upon their way of application. While hair fixatives are applied to the hair before—and aiding in—the setting, the lacquers are sprayed onto the hair after the coiffure has been finished. Colloid substances are in both cases used as binders and film formers for the hair. In fixatives they are mostly gums, in hair lacquers shellac or resins, and as the hair lacquers must be sprayed, they must be of low viscosity, while the fixatives are of the gel-type or high viscous lotions.

Gums, shellac and resins are usually rather brittle substances, which have to be plasticized to avoid the unpleasant flaking of the film, which in bad cases looks like dandruff. Here again we can take profit with glycerine: as a plasticizer and softener for the film-building substance, as a conditioner for the hair, so it looks more supple and is easier to set, and as an aid in redissolving the film, either for resetting of the hair with a moist comb or in a desired removing of the film.

The hair fixative is a very nice semi-gel, easy to apply and really corresponding to its name of fixative:

High viscosity sodium alginate	9	Ethanol 96%	15
Glycerine	3.2	Perfume (water soluble), colour preservatives	q.s
Water, to make	100		

Disperse the alginate in alcohol and glycerine. Add the water and when smooth, the perfume. It is most convenient to fill it into wide necked bottles immediately after the mixing, as it gets pretty viscous in a couple of hours.

DRESSINGS. In the last decade, the old fashioned liquid brilliantines (consisting mainly of vegetable and mineral oil) have been outclassed by the cream-type hair dressings, principally manufactured as the well known borax-cold creams, the difference being a lower melting point of the wax-oil mixture and eventually addition of further emulsifiers. Such creams are virtually mixed-phase emulsions, with a tendency to drying when exposed to the atmosphere, so a glycerine addition will be of benefit for keeping qualities. Further it will be of aid in the manufacture of oil in water creams, manufactured with the modern synthetic polyglycol ether-emulsifiers.

Here is a formula for an oil-in-water cream, easy to spread, giving a nice lustre to the hair without being too greasy. The glycerine will, together with the emulsifiers, help re-emulsification of the fatty substances during shampooing, an advantage which is often missing in hair creams

and almost always absent in liquid brilliantines. The cream is suitable for packing into tubes, but because of the nonionic emulsifier, the preservative must be selected very carefully.

HAIR CREAM (dressing, grooming cream)

Stearic acid	6	Isopropyl myristate	12
Spermaceti	6	Light white oil	20
Glyceryl monostearate	2	Triethanolamine	0.8
Ethoxy lauryl ether	2	Glycerine	4.2
White petrolatum	6	Water, to make	100
Lanolin	2	Perfume, preservative	q.s.

Melt together the waxes and oils; mix the water phase. When both phases at a temperature of 70°, gradually pour water phase into oil-phase, while stirring slowly. Continue stirring till cool; add perfume at ca. 45°C.

(Continued from Page 1)

HEAT-WAVING, DYEING, REMOVING AND STRAIGHTENING

by Dr R. Heilingotter

Ammonium sulfite, 22° Be	1.0	Triisopropanol aminoleate, 25%	2.0
Ammonia, 0.910	20.0	Nekal	0.1
Glycerine 28° Be	2.0	Water, dist.	73.0
Polyethylene glycol	2.0		

The addition of glycerine to cold-wave lotions has not been found as necessary because of the self-softening action of the active ingredients of such solutions, but some home-wave lotions contain thioglycerine as active agent in alkaline medium. Glycerine, in this case, is used as raw material for the synthesis of the thio compound.

Recently, weakly acid or nearly neutral cold-wave lotions have been introduced. One of these preparations (3) uses thioglycerine without any addition of ammonia or another alkali, at a ph of 4 to 6. Thioglycerine can be prepared from glycerine-glycid (epichlorhydrin) and hydrogen sulfide or barium sulfide, according to Smith and Sjoeberg (4) or by Morell (5) from a mono-chlorhydrin with potassium sulfide or hydrogen sulfide.

Acid cold-wave lotions may also consist of mercaptan carbonic esters, containing at least one hydroxyl group in the molecule, at a ph of 4 to 7, according to Richter (6). In this case glycerine-monothioglycolic ester and/or similar other esters are used and glycerine is necessary as raw material to produce this compound.

A completely different way to produce heat-permanent waves eliminates electrical energy to obtain the curling effect together with usual alkaline heat-wave lotions by replacement of the electrical heat by chemical heat. Use is made of combinations of chemicals to give sufficient heat by chemical exothermal reaction, if moistened. Besides other combinations an oxidative reaction between permanganates and glycerine or other oxidizable substances, has been found as particularly effective. This has been described by Bonat (7) and Francis (8).

HAIR DYEING. Glycerine is often used in hair-dyeing preparations, for example, in a "Henna liquid shampoo" described by Jannaway (10):

Soapless shampoo base	20 to 30%	Lawsone, synthetic	0.08 %
Lactic acid	0.5 %	Alcohol	10.0 %
Glycerine	5.0 %	Water, to make	100 %

Glycerine has been of special importance to the manufacture of metallic hair-dyes. An addition of glycerine to hair restorers is usual to keep them humid during application. Creamy preparations of this kind are intended to provide an additional amount of glycerine, according to Jannaway (11):

Emulsifying wax	10 g.	10 g.	Copper chloride	0.5 g.	—
Cetostearyl alcohol	5 g.	5 g.	Lawsone, synthetic	0.02g.	—
Liquid paraffin	8 g.	— g.	Indigo, soluble	0.1	—
Glycerine	5 g.	6 g.	Water, dist.	68.0	75 g.
Lead acetate	3.4 g.	4 g.			

Modern oxidation hair-dyes are today mostly manufactured as cream or jelly in a consistency suitable for tube filling. The cream hair-dyes have been the first of this type and have been introduced on the market by Stroher (12). As a cream base, glyceryl monostearate has been used and many imitations utilize the same emulsifier, alone, or in combination with other fatty compounds able to form an emulsion. Glycerine is necessary to produce glyceryl monostearate. This emulsifier is not only in use to prepare cream oxidation hair-dyes but also to produce cream color rinses.

Liquid color rinses, which have the same duty, to give a light coloring effect to the hair, are prepared with addition of glycerine, conforming to a formula, given by Jannaway (13):

Chamomile extract	12.0 g.	Glycerine	2.5 g.
Rhubarb, conc. infusion	3.0 g.	Chamomile oil or compound	0.5 g.
Lawsone, solution 1%	2.0 g.	Water	80.0 g.

HAIR REMOVING. Glycerine is also used in depilatory preparations in appreciable amounts; they are mostly offered as cream products. Glycerine gives softness and suppleness, preventing drying during application to the skin. In general depilatories are not declared skin compatible preparations since they attack not only the hair, but also the skin, making it rough and brittle. Glycerine has to counteract this disagreeable, secondary effect. The following formulas, according to Winter (14), show that glycerine is useful in considerable amounts:

Strontium sulfide	30	27	Lanolin, anhydr.	—	8
Calcium sulfide	—	3	Glycerine	10	8
Calcium carbonate	15	—	Water	30	25
Gum tragacanth	—	0.3			
Starch	15	5		100	76.3

Also in the modern cream depilatories based on thioglycolates glycerine is used in appreciable quantities, as the formula of Keithler (15) shows:

Calcium thioglycolate	6%	Sea Kem Type 11	2%
Carbowax 6000	9%	Alcohol	5%
Glycerine	10%	Water	47%
Zinc oxide	20%	Perfume	1%

HAIR STRAIGHTENING. It is a fact that individuals with straight hair want curly hair and the individuals with curly hair believe straight hair to be more desirable. But to the great percentage of individuals with natural curly hair, hair straighteners have become today more and more important. An ancient method was that of plastering down the hair by the use of gums or resinous-fatty vehicles. Later on an alkali type of straightener came into use; these formulas contain glycerine:

Sodium hydroxide	4	10	Oleic acid	—	5
Glycerinmonostearate	16	—	Glycerine	5	5
Stearic acid	—	15	Water	75	65

In modern preparations, thioglycolates have been used for hair straightening. Such preparations contain 1 to 12 per cent thioglycolic acid; sufficient alkali, for example ammonia to form ammonium thioglycolate; an organic amine, such as ethanolamine to produce sufficient alkalinity; ingredients able to give viscosity and adhesion, such as alkylcellulose, alginates, polyvinyl alcohol, Carbowax and suitable other products (16). Another suggestion by Morelle (17) uses thiolactic acid together with a water soluble non-toxic alkali, jelly forming compounds and water. In both formulas an addition of glycerine seems to be desirable.

Bibliographies available upon request.

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Continued from page 46

These properties must be excellent.

4. Fastness against Hair Dyes

This seemingly paradoxical demand is of great importance. In order to avoid dye addition at the already predyed parts when dyeing the regrowth, partial removal of the dye must be possible by the dyeing agent itself.

5. Fastness against Reductive and Oxidative Decolorants

In the case of mis-dyeing, removal must be possible. This is accomplished to some extent with reducing agents as sodium dithionite, sodium sulfoxylat, etc., however, results are better with bleaching agents.

II. Hair Color Toners

As hair color toners are used to achieve only fashionable effects or to treat only slightly grey hair the demands for fastness properties are not as exacting as with hair dyes. Light and washing fastness may be reduced, whereas fastness against cosmetic treatments, wetting, sweat and rubbing must also be good.

Summary

Dyeing living human hair is a special coloring process. The chemist who is familiar with textile dyeing faces a lot of entirely new problems in human hair dyeing.

An investigation of textile dyeing shows that the two phenomena controlling the dyeing process—diffusion of the dyestuff into and its fixing in the fiber can be controlled to a relatively large extent by choosing suitable dyestuffs and working conditions.

When applying this knowledge to the dyeing of human hair, one will easily see that the coloring possibilities are considerably reduced here because of the necessary adaption to physiological conditions, the variability of human hair and the continual hair growth.

Up to this day it is only the oxidation dyes which are able to meet the customer's specific demands for a hair dye, while other categories of dyes can be used only to a limited extent for obtaining color effects by superficial absorption.

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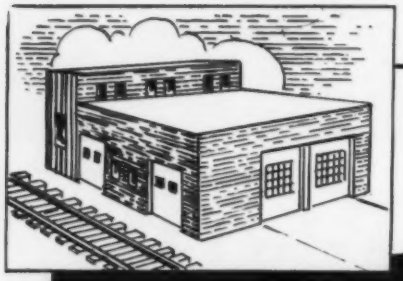

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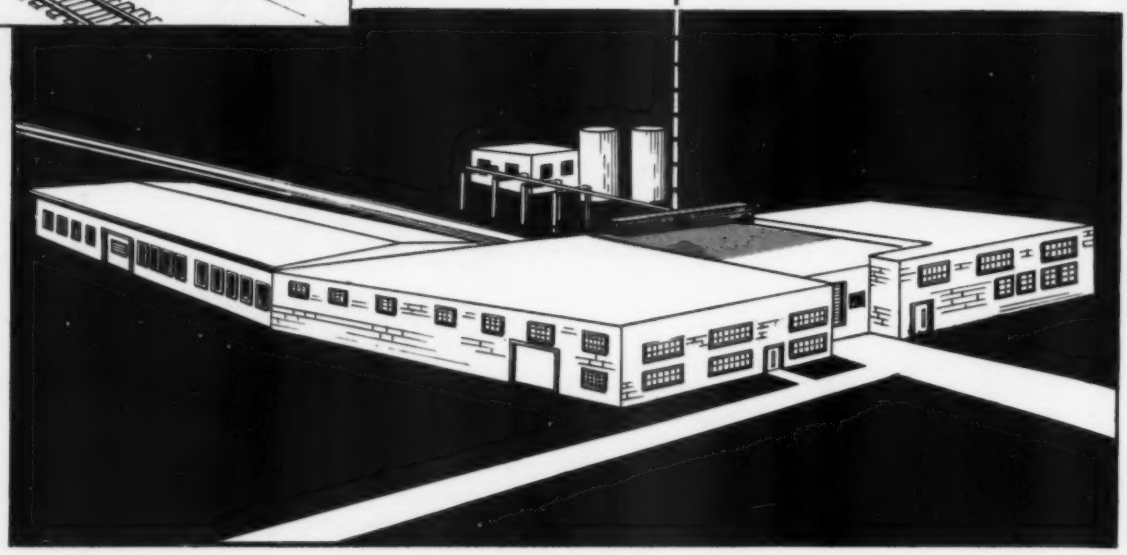

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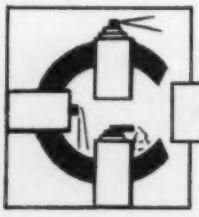

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Danville, Illinois

Fundamental Research for the Composition of Lipstick Substances

By Gustav A. Nowak

Development of lipsticks is made mostly by experimental methods. Only when it is believed that a stick has been found that meets the requirements of being color fast, the melting point and other standards set by the technicians and by their research methods, then only the product is ready to be tested by the consumer. There are many instances that technical shortcomings of the stick appear only after a longer storage or as a result of extraordinary climatic conditions.

The problem of developing a series of new lipsticks begins with the contemplation as to which bromo acid solvents come actually into consideration. It is the type, the quantity and the combination of eosins and of their solvents on which the quality, fastness of the lipstick, depend.

Furthermore: the composition of the lipstick, in other words the wax mixture, depends from the selected bromo acid solvents. Imcompatibility between the solvents and wax base used, leads sooner or later to a separation, to an "exudation" of the solvent.

Among the appropriate bromo acid solvents are:

Glycols and their esters and/or their ethers, for example diethyleneglycolmonoethylether (APV, Carbitol). When we use them we must take into consideration that hexylene glycol dissolves the bromo acids, but has a bitter taste. Carbitol is even better, but it has an unpleasant taste, too. On the other hand, propylene-glycol has a sweet taste and can be used as a bromo acid solvent in lipsticks.

While castor oil has only a slight dissolving capacity for bromo acids, we hardly can renounce using castor oil as an ingredient of lipsticks.

The esters of sebacic and adipic acids (diethylsebacate, cetylsebacate, iso-adipate are good solvents for bromo acids; they all have a soapy, slightly burning taste, though. Technically they may be used to good advantage if applied in a not too high dosage, because they represent universal solvents, which are soluble both in mineral and fatty oils and are compatible with alcohols.

Oleyl alcohol possesses sufficient dissolving capacity for bromo acids and it is highly recommended.

Tetrahydrofurfuryl-alcohol and esters thereof dissolve bromo acids very well; they have a bitter taste, though.

The fatty-acid-alkylol-amides, particularly the monoalkylol-amides of non-saturated fatty acids, which are being marketed under the name of "Loramin", have, too, a very good dissolving capacity for bromo acids and are compatible with the customary wax components. Their wax-like consistency requires an examination to determine the compatibility with other (liquid) bromo acid solvents. Very disturbing is the pepper-like taste and throat discomfort they cause.

The following table shows the solubility of tetrabromo-fluorescein according to percentage by weight at 20° C:

propylene-glycol		1.6
hexyl-glycol		5.0
carbitol	appr.	20.0
diethyl-sebacate		1.3
iso-adipate		1.4
castor oil		0.4
oleyl-alcohol		1.0
tetra-hydro-furfuryl-alcohol		18.0

A good dissolving power for bromo acids have the liquid polyethylene-glycols and their higher-molecular, solid modifications, the carbowaxes. They leave, however, (in particular the liquid ones) a pentrating taste. In addition to that their water solubility is very high and as a result sometimes even the teeth and the areas around the mouth become colored through the bleeding of the lipstick color.

When we take the taste into consideration, there remain only the following solvents:

Propylene-gylcol, oleyl-alcohol, castor oil, ester of the sebacic acid (diethyl-sebacate) and the ester of the adipic acid (iso-adipate) as well as in lesser quantities the alkylolamides.

There still remains the examination of the compatibility of these solvents with the customary wax components. For this purpose we have melted the solvents, 1 & 1 respectively, with various waxes. We arrived at the following:

A. beeswax + propylene-glycol = 1 + 1: soft-waxy, homogenous substance
beeswax + oleylacohol = 1 + 1: soft-waxy, homogenous substance
beeswax + diethyl-sebacate (or iso-adipate) = 1 + 1: soft-waxy, homogenous substance
beeswax + castor oil = 1 + 1: soft-waxy, homogenous substance

B. alkylolamide (Loramin OM-101) + propylene-glycol = 1 + 1: soft-waxy, homogenous substance
alkylolamide (Loramin OM-101) + oleyl-alcohol = 1 + 1: soft-waxy, homogenous substance
alkylolamide (Loramin OM-101) + diethyl-sebacate (or iso-adipate) = 1 + 1: soft-waxy, homogenous substance
alkylolamide (Loramin OM-101) + castor oil = 1 + 1: soft-waxy, homogenous substance

C. lanolin + propylene-glycol = 1 + 1: *no* homogenous substance; the propylene-glycol separates
lanolin + oleyl-alcohol = 1 + 1: very soft, fully homogenous substance
lanolin + diethyl-sebacate (or iso-adipate) = 1 + 1: very soft, fully homogenous substance
lanolin + castor oil = 1 + 1: soft, lanolin-like consistency, fully homogenous

D. ozokerite + propylene-glycol = 1 + 1: *no* homogenous substance; the propylene-glycol separates
ozokerite + oleyl-alcohol (or iso-adipate) = 1 + 1: homogenous, waxy substance homogenous, waxy substance
ozokerite + diethyl-sebacate = 1 + 1:
ozokerite + castor oil = 1 + 1: waxy, homogenous substance; castor oil separates insignificantly.

E. ceresin + propylene-glycol = 1 + 1: waxy substance; the propylene-glycol is not completely absorbed. A small quantity of propylene-glycol settles.
ceresin + diethyl-sebacate (or iso-adipate) = 1 + 1: fully homogenous, waxy substance
ceresin + oleyl-alcohol = 1 + 1: fully homogenous, waxy substance
ceresin + castor oil = 1 + 1: castor oil separates just a little bit.

F. carnauba-wax + propylene-glycol = 1 + 1: not homogenous, propylene-glycol settles
carnauba-wax + oleyl-alcohol = 1 + 1: homogenous, waxy substance
carnauba-wax + diethyl-sebacate (or iso-adipate) = 1 + 1: homogenous, waxy substance
carnauba-wax + castor oil = 1 + 1: homogenous, waxy substance, showing a bright surface ("mirror").

G. hydrogenatum (hydrogenated)
peanut oil + propylene-glycol = 1 + 1: propylene-glycol settles below; two layers are formed.
peanut oil + oleyl-alcohol = 1 + 1: thin, not fully homogenous substance; oleyl-alcohol separates above.
peanut oil + diethyl-sebacate (or iso-adipate) = 1 + 1: thin, not fully homogenous substance; diethyl-sebacate separates above a little.
peanut oil + castor oil = 1 + 1: soft, homogenous substance of butter-like consistency.

H. glycerin-monostearate + propylene-glycol = 1 + 1: fully homogenous, waxy (not self emulsifying)
glycerin-monostearate + oleyl-alcohol = 1 + 1: fully homogenous, waxy
glycerin-monostearate + diethyl-sebacate (or iso-adipate) = 1 + 1: fully homogenous, waxy
glycerin-monostearate + castor oil = 1 + 1: fully homogenous, waxy

J. cetyl-alcohol + propylene-glycol = 1 + 1: homogenous, waxy mass
cetyl-alcohol + oleyl-alcohol = 1 + 1: homogenous, waxy mass
cetyl-alcohol + diethyl-sebacate (or iso-adipate) = 1 + 1: homogenous, waxy mass
cetyl-alcohol + castor oil = 1 + 1: homogenous, waxy mass

K. Spermaceti + propylene-glycol = 1 + 1: propylene-glycol settles below; not homogenous
Spermaceti + oleyl-alcohol = 1 + 1: homogenous, waxy-brittle substance
Spermaceti + diethyl-sebacate (or iso-adipate) = 1 + 1: homogenous, waxy-brittle substance
Spermaceti + castor oil = 1 + 1: homogenous, waxy-brittle substance

L. absorption base (Protegin) + propylene-glycol = 1 + 1: propylene-glycol separates, but not as intensely as lanolin
absorption base (Protegin) + oleyl-alcohol = 1 + 1: homogenous, soft like butter subtance
absorption base (Protegin) + diethyl-sebacate (or iso-adipate) = 1 + 1: homogenous, soft like butter subtance
absorption base (Protegin) + castor oil = 1 + 1: not fully homogenous, very soft substance

M. Petrolatum + propylene-gylcol = 1 + 1: propylene-glycol separates below.
Petrolatum + oleyl-alcohol = 1 + 1: homogenous, soft substance
Petrolatum + diethyl-sebacate (or iso-adipate) = 1 + 1: homogenous, soft substance
Petrolatum + castor oil = 1 + 1: homogenous, soft substance

N. cocoa butter + propylene-glycol = 1 + 1: propylene-glycol settles
cocoa butter + oleyl-alcohol = 1 + 1: homogenous, liquid mass
cocoa butter + diethyl-sebacate (or iso-adipate) = 1 + 1: homogenous, liquid mass
cocoa butter + castor oil = 1 + 1: homogenous, liquid mass

Discussion about the results

If we use propylene-glycol as a solvent for bromo acids, we best combine it with alkylolamides. The lipstick substance in this case must consist predominantly of beeswax, cetyl-alcohol, glycerin-monostearate (not self emulsifying) and a smaller quantity of ceresin. Oleyl-alcohol is compatible with this substance and we may subsequently combine it as a solvent of bromo acids together with the mentioned ingredients.

The esters of the adipic and sebacic acids (for example diethyl-sebacate and iso-adipate) are compatible (with the exception of hydrogenated peanut oil, which performs very poorly as the basis for lipsticks) with all usable wax components of the lipsticks. They are excellent, universal solvents.

A universally compatible wax component in the lipsticks is cetyl-alcohol, which harmonizes not only with propylene-glycol but also with diethyl-sebacate, oleyl-alcohol and castor oil.

If we choose for the bromo acid solvent a combination of diethyl-sebacate, oleyl-alcohol and castor oil, the following raw materials are appropriate for the purpose of obtaining the lipstick substance:

Lanolin, beeswax, Loramin, carnauba-wax, cetyl-alcohol, ozokerite, Protegin, petrolatum, glycerin-monostearate (not self emulsifying) and a smaller quantity of ecresin, spermaceti (cetaceum) and cocoa butter.

Castor oil harmonizes best with carnauba-wax together with which it produces a bright surface ("mirror") and as a result we achieve by this combination and by adding resins (for example colophony) a nice and shiny lipstick. Castor oil may be combined with advantage also with lanolin and hydrogenated peanut oil.

One more word regarding the use of cocoa butter in making lipsticks; the intrinsic low melting point of cocoa butter at 30 to 35° C is further reduced by adding oils so that at room temperatures we obtain liquid mixtures. We cannot expect the cocoa butter to produce any stiffening effect of the lipstick. On the contrary, in heating up the lipstick substance comprising cocoa butter, we witiness the change of the cocoa butter into an unstable shape with a setting point at 15 to 17° C. This unstable modification (β-Form) of the cocoa butter with a melting point below room temperature does not occur, if we do not permit the melting and casting temperature of the lipstick substance to exceed 36° C. Since this is practically impossible, the usefulness of a cocoa butter addition to the lipstick substances is negligible, and, as far as greater quantities are concerned, even dangerous, because the mass becomes too soft. Furthermore the setting of the lipsticks in the molds may be delayed. Sedimentation of the pigment colors may well be the result.

The setting point of cocoa butter lies 12 to 13° C. below the melting point. Furthermore, cocoa butter contracts very little when setting, so that the lipsticks remain stuck to the molds.

In general the best universally common dissolving and combining features are those of the adipic and sebacic esters.

A New Market—

Specialty Chemicals For The Home Swimming Pool

By A. Haldane Gee, Ph. D.
Foster D. Snell, Inc.

Before the current season is over, there will likely be 250,000 residential swimming pools in operation, the biggest mixing tank ever for the home chemist. All need additives, for esthetic and sanitary reasons, just like public and institutional installations.

For the large pool, where chlorine is usually employed, the treatment methods have been well worked out, and the equipment is standardized and reliable. Chlorine, in one form or another, is relatively inexpensive. National servicing is available, for example through Wallace and Tiernan, Inc., leading manufacturer of chlorinating equipment.

For the home pool, there is a definite demand for specialty products where convenience and other advantages are more important than economy. It is true that there are some inexpensive products available for the home pool, but there are usually problems in application since few home pools have completely automatic equipment.

The outdoor pool, whether "free form" or tank type, is becoming an ever more prominent feature of the landscape, as many air travelers have observed. Perhaps one third of the nation's private residential pools are in California, but the building of permanent pools is now expected to go ahead at a faster rate in the northeast, according to the latest survey of Swimming Pool Age, business paper of the pool building and maintenance industry, which further forecasts a census of 2,000,000 in-the-ground pools within 10 years.

Big potential market

About three-fourths of the residential pools range from 15 x 30 feet to 20 x 40 feet, according to the Swimming Pool Age survey. Based on an average size of 20,000 gallons, and with standard chlorination treatment levels, daily over a minimum two months' season, the owners of private pools may use up 1,500,000 gallons of laundry bleach or 1500 tons of chloride of lime. Although these may represent modest quantities in terms of heavy chemical industry, there is every reason to believe that the real market lies ahead—larger, more discriminating, definitely receptive to luxury products.

In the larger swimming pool, virtual disinfection can be accomplished with either chlorine gas or hypochlorite metered into the circulating system. For pools of from 100,000 to 300,000 gallons or larger, chlorine gas has been used almost universally because of its low cost and ready availability. For pools below 100,000 gallons, it may be more convenient to use sodium hypochlorite, although the cost in comparison with chlorine gas may depend on shipping costs and the geographical area.

For most home pools, 10,000 to 30,000 gallons, sodium hypochlorite can be used, although the records show that only about 10 percent of the permanent residential pools were equipped with hypochlorinators, up to this year. The majority of the home pools, if chlorinated, were treated with laundry bleach from the bottle, or with calcium hypochlorite added from small bags or in some other extemporaneous way.

Sanitary requirements

Regardless of the form in which it is added, chlorine should be maintained in a pool at a minimum of 0.6 parts per million (ppm) of free, available chlorine. It is possible also to carry 2 ppm or even 3 ppm with certain advantages, and under the right conditions, without building a chorine odor or causing the swimmers eye irritation. In this range, a prompt germicidal action can be expected, so that under any normal bathing load, the pool water is maintained at a sanitary level equivalent to that of drinking water. The proper use of chlorine will also restrict the growth of algae.

Now if chlorine is so certain and so universally used, the question arises as to the real need for other products for the home pool. The answer is in the amount of management or supervision necessary to maintain the proper level of free chlorine, which cannot be determined at all from the amounts added. Enough chlorine must be added initially to satisfy the chlorine demand of the water and to provide the required amount of free available chlorine. The free available will then be consumed as the pool is used by bathers. Also, chlorine will be lost on standing, especially in an outdoor pool in the sunshine.

The only way to control such a constantly changing situation is by testing the pool water chemically, at least once a day, oftener if the pool is used heavily. This the commercial or professional pool operator is well equipped to do—must do if he is to comply with health requirements. The home pool owner must be prepared to do the same thing if he wants to use hypochlorite properly, otherwise the treatment will swing between a low, ineffective level and a too high, unpleasant level—seldom right. Proper control can, however, be maintained by the home owner with elementary chemical sense—sufficient to enable him to use a simple colorimetric test kit properly.

Along with its sanitary function, chlorine properly used will help to maintain the clarity of the pool water and consequently its natural blue color. But this brings in other characteristics, including relative hardness and alkalinity control. These factors can be regulated by separate additives, when necessary, although proper use of them calls for still further tests. The alkalinity, best maintained at 7.2 to 7.8 on the pH scale, can be controlled with a colorimetric test kit and additions of soda ash, alum, or in the case of an unduly alkaline water, with mineral acids. The relative hardness is best maintained at 50 to 100 parts for a chlorine treated pool. Adjustments for hardness, however, may be based on an occasional hardness test, which will usually indicate a constant treatment ratio if the pool is regularly filled with water from the same source of supply. All of this control is relatively simple for the pool owner who is prepared to go to the necessary trouble. To supply those who are not so minded is the purpose of other additives that need less care and attention. A product may be suitable for the residential pool, even though it may be inadequate or uneconomic for the public pool.

The ideal product

The home pool owner would like, and undoubtedly would pay for, a product that he could add once a week or at most once a day, in fixed amount, without testing, and easily distributed throughout the pool. This should maintain the water in clear and sanitary condition, without unpleasant odors and without causing the bathers discomfort or irritation. This product has yet to be developed, although some of the available additives come closer than others.

In the residential pool, the lighter bathing load and the less frequent use—seldom continuous—justify the use of additives at a moderate or sanitizing level, rather than at a strong germicidal or disinfectant level. Without any kind of sanitizing agent, the users of a pool are sharing common bath water, which is repugnant even to members of a family, as well as a degree of intimacy inappropriate to even the most informal host and guest relationship, when there are visitors. On the other hand, a chlorine treatment that will kill in minutes, as well as coping with an appreciable organic load, is not required. A treatment that will maintain clear water, and will restore the sanitary quality of the water following incidental contamination, will frequently be adequate even though several hours may be required for bacterial count reduction, or even overnight. Conversely, an additive that will maintain its activity over a prolonged period is more desirable for the home pool than one with a strong action that may "run down" in a short time.

The established additives for the home pool—other than hypochlorite—include organic chlorine compounds, other halogens, quaternary ammonium compounds, and acid treatment to some extent. A newcomer with a good potential is one of the more recently available oxidizing compounds that has been used in new scouring compound formulations. Agents rather in the gray area of utility for the pool application include silver, ozone and ultraviolet irradiation.

Among the chlorine combinations encountered sooner or later in swimming pool management are the chloramines, a term used to cover a class of compounds and also specific trade products. Any chemical compound containing chlorine attached directly to nitrogen is a chloramine. The simplest form is produced in the pool when chlorine combines with ammonia from plant sources or from animal sources.

This complicates the control of the pool, reduces the free available chlorine, accentuates the odor problem and may promote the growth of plant life as a secondary effect. These undesirable results can be minimized by frequent retesting of the free available chlorine in the pool, and chlorination to the higher levels.

A specific related compound is para-toluene chlorosulfonamide, sold under the trade name Chloramine-T. This is a useful disinfectant employed especially in dairy plants and restaurants. It can form a reservoir of disinfectant from which chlorine is released slowly. There are, however, offsetting limitations which probably account for the fact that Chloramine-T is not usually included in the list of accepted, established swimming pool sanitizing agents.

Isocyanurate

A newer chlorine compound that is finding some acceptance is sodium dichloro-isocyanurate, which also has a high yield of available chlorine. This also is a "bank" type of chlorine source providing chlorine over an extended period. This product was set back last winter by a report from California in which possible mucous membrane irritation or possible general poisoning effects were suggested. On the basis, however, of a more detailed study, it has been concluded that isocyanurate should be safe in amounts up to 100 ppm. Increased use of this relatively stable product may accordingly be expected.

Still other organic chlorine compounds are understood to be under investigation, as part of the search for a surer, more convenient material for the small pool owner, but none of these has yet appeared to have reached even the stage of full scale pool testing in a swimming pool.

Of the other halogens, bromine has been used commercially while iodine has been used in various forms, generally on an investigational basis. Bromine has well established antibacterial properties, but the handling of liquid bromine presents some hazard even for the chemical worker. Iodine is more easily handled and its germicidal properties are well known to the layman. Three ways of using iodine are as iodine-iodide solution, as iodine dissolved in water solution, and as iodine released from iodide in the pool by additions of hypochlorite. In the third method, the iodide is added when the pool is first filled. The recommended free iodine range is 0.2 to 0.6 ppm. Claimed advantages are minimized odors and less eye irritation whereby bathers prefer iodine treatment over chlorination. With the possible exception of the "iodide bank" method, the cost of iodine treatment would undoubtedly be higher than that of chlorine treatment. The possibilities of the relatively new organic iodine complexes have apparently not been explored in swimming pools.

Departing from the halogens, two entirely different types of disinfectant materials are used commercially —one type compatible with chlorine and the other not. On the West Coast, there has been some application of sulfamic acid, which has an established place in home and food plant sanitation. It has been used to dissolve milk stone in dairy plants, and as an ingredient of acid toilet bowl cleaners. The use of acids in the pool is a complete departure, however, calling for reconsideration of the mild hardness and alkaline pH requirements essential for satisfactory chlorination.

Quaternary ammonium compounds

The chlorine-compatible types are the several quaternary ammonium compounds offered by at least three manufacturers, although usually for the control of algae. Here competition enters strongly, just as in the case of the various classes of products sold for use in disinfectant formulations for home, industrial and institutional use. The chlorine manufacturers contend that proper chlorination will control algae as well as accomplishing disinfection. The quaternary ammonium producers claim algae control without some of the problems of chlorine. The QAC's are usually valued for their high potency antibacterial effects, in other applications. They should have a potential in swimming pools beyond the function of algae control, especially in soft water situations, but there is need here for further information on the merits and demerits, under supervised use conditions.

For algae control primarily, copper sulfate remains one of the old and reliable agents. Its antibacterial effects are, however, relatively weak, hence copper sulfate is more a useful agent for the private pond than for the private pool.

A material relatively untried in the swimming pool field but finding increasing applications in products for the home is potassium monopersulfate, the active agent in home bleach formulations sold under the name of Oxone. Oxone is used also in scouring compounds, laundry machine formulations and stain removers. Monopersulfate has many potential advantages for the home pool, including absence of odor, ease of application and sustained action. The action is not as rapid, however, as that of chlorine, hence Oxone is not suitable for the public pool with the heavy bathing load.

On the gray list of pool treatments are three agents promoted from time to time: silver in one form or another, ultraviolet irradiation, and ozone. Each may have some value, although none seems to have survived the combined tests of rigorous proof, consumer acceptance and commercial success.

Silver has been added to pool water electrolytically and on the surface of granules. It is enjoying a current vogue in bacteriostatic treatments offered for a variety of consumer products. The ultraviolet process is well established for the treatment of water in thin films, for example in soft drink manufacturing plants. Ozone, also, has recognized industrial applications. But none of these has qualified as technology's unique gift to the home pool owner.

Legal requirements

Claims for practically every pool additive are subject to review by regulatory authorities, Federal, state, local. Any product with sanitizing or germicidal claims, sold interstate, is subject to registration by the U. S. Department of Agriculture, on the basis of formulation, claims and directions, effectiveness and general safety in use. Some states have parallel re-

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quirements for materials sold in their boundaries. Others, also many municipalities, have recently enacted precautionary labeling requirements for hazardous substances, which apply to a number of pool additives in concentrated form.

New regulations and legal interpretations will bring more products within the scope of these laws. A "fungicide" cannot be sold interstate under a trade name, without disclosure of active ingredients. A product usually sold for a less closely regulated use may be subject to additional requirements if knowingly channeled into swimming pools. Example: hypochlorite, although used primarily as a home bleach, must meet in Florida the requirements applying to pesticides, if sold to swimming pool owners.

While additives for sanitary control are in process of development, the situation to be controlled is subject to some degree of evolution. The classical—and still recognized—bacteriological index of sanitary quality is essentially the same as used for drinking water supplies. The water should be substantially free from colon bacteria, which are indicative of intestinal contamination. The normal colon organism is itself bland, but its presence in any count above the minimum detectable level is a basis for suspecting the tandem presence of potentially dangerous organisms, especially typhoid. There is increasing question among bacteriologists and public health officials as to whether the colon index is an adequate one. The colon organism in variant form has been known to display pathologic effects in man. Of more concern, however, are the coccus forms, especially antibiotic resistant Staphylococcus which has been appearing everywhere as an unfortunately too real bogeyman. How susceptible or resistant these latter day menaces are to standard pool treatments is something that health authorities are studying intensively. There may in consequence be a stiffening up of requirements for all pools, public and private.

Some pool additives are less involved with sanitation and consequently less subject to regulation. Alkalinization, for example, can be accomplished with briquets of soda ash placed directly in the pool. Flocculation of sediment can be assisted by the addition of waterworks alum. But these agents also influence the effects of the sanitizing agent, especially chlorine, and may determine whether the pool needs lesser amounts of germicide or greater amounts. With presently available materials, the pool owner will still need to make some of his own simple tests, if he wants to be sure how acceptable the water is. And by the same token, the time is some distance away when the pool can be given a single, one-shot seasonal treatment, like putting permanent antifreeze in the radiator.

Water circulation

The permanent home pool, at grade, is usually equipped with filtration equipment, hence some circulation of the water is assured even when the pool is not being used. The above grade or flexible wall pool is usually not so equipped, hence the mixing in of additives has to be done with paddles or by the efforts of the bathers. But regardless of the method, the extent of agitation and the turnover time in circulating systems are factors that have to be taken into account in using additives. There may be here a new field of usefulness for the portable mixer, for use in pools not equipped with metering devices for additives.

There are two uses for germicides in conjunction with swimming pools that are not directly related to treatment of the water. The "antiseptic" foot bath was a common accessory in the club pool at one time, for the intended purpose of preventing the spread of athlete's foot, the common fungus-caused skin disease. Experience showed, however, that such foot baths frequently had lost their activity and were loaded with debris. Furthermore, the contact with the feet was too brief for any useful result. The preferred method of controlling such skin fungi is by the observance of good sanitary practices throughout the swimming pool premises, including the periodic treatment of deck areas and locker room floors with suitable antiseptics, used at sufficiently strong levels.

The second related use of germicides is also a surface treatment, for the interior wall and floor of the pool for preventing adherent algae growths. These agents may be incorporated in vinyl liners or in paints. They will prevent build-up on the treated surfaces, although they cannot be expected to convey any beneficial properties to the water. Among the more successful compounds for this purpose are organic mercurials, especially phenyl mercuric borate.

Luxury products

From the obligatory additives for the pool one can proceed into treatments that have sensory appeal as their sole purpose. For the esthete, there are color and taste possibilities. The simplest variation is the use of colored paint, available in 16 different shades. There are also possible dyes for the water, although the choice of colors is rather limited if one avoids colors suggestive of physiological processes. Possibilities are fluorescent pink or an aqua shade short of weedy green.

The addition of a bouquet to the water has been given some passing attention by one of the essential oil houses which supplies a major share of the fragrances used in bath oils and other bathing preparations. For general spring appeal, a light floral odor has been proposed, applied on the surface of the pool. For summertime, a pine scent suggestive of the mountains would be feasible. For fall, chrysanthemum or apple essence have been suggested. For winter bathing, however, speculation has run to a brandy or bourbon flavoring, with the degree of realism dependent largely on the pocketbook.

In all such luxury additions, attention would have to be paid to the other, working additives, which might cancel or modify undesirably the purposely added odors. The formulator who is developing products for the private pool owner should, however, keep in mind the simplest additive of all available for the residence pool if it is not too large—more fresh water. A cleaning and refilling with fresh water (like fresh air) will be simpler than endless corrective additions—but every refilling is an opportunity to sell a new charge of basic treatment.

Contribution to the Identification of the Estrogen Activity of Hops

By Dr. A. Zenisek and Ing. J. Bednar

During recent years the biologically active substances from animal and vegetable tissues are being used to an increasing degree in modern skin care cosmetics. The purpose of applying these substances is to prevent the premature aging of the skin by improving its tone, the blood circulation in the skin, its degree of hydration and regenerative ability. In their review on active plant substances Perner and Zenisek (1) draw attention to substances with a hormonal, and especially an estrogenic activity (e.a.) which are known as *phytohormones* in world literature.

Already in 1926 Loewe (2), Dohrn et al. (3), and Fellner (4) report that certain plant substances develop estrus in animals. Although Butenandt and Jacobi (5), and Skarzynski (6) isolated substances identical to estron and estriol from certain plants (willow catkins, palm kernals), it was soon evident that the e.a. of plants need not to be related only with substances of steroid structure, but also to various other substances with a different structure. Schoeller (7), for example, isolated from the papilionaceous plant Butea superba, a strong estrogen of an unknown constitution, with chemical and physical properties which resemble no known plant estrogen.

In the clover, Trifolium subterraneum, Bradbury and White (9) discovered a weak estrogen, genistein (4, 5, 7-trihydroxyisoflavon). The detailed report of these authors on the e.a. of 50 plants shows that the strongest plant estrogen is the above-mentioned phytohormone from Butea superba, whose e.a. amounts to 500-900 i.u./gr.; however, this report does not mention the e.a. of hops.

The paper of Kock and Heim (11,12) inspired us to study the phytohormones of hops. These authors discovered that the extract of hop-cones contains 300-3000 i.u./gr., but lacked the means to identify the substance which causes the e.a. The healing and

rejuvenating effect of brewery cold sludge baths has been known for ages. In Germany the "Trubbad" was actually called "Jungbrunnen". According to Heilmann (13) cold sludge contains as much as 30% of substances from hops. Because of the healing effect of these baths, in 1406 King Wenceslas IV allowed the baths to use the hop-cone in their coat-of-arms. Today, these baths are used in Germany not only in the treatment of certain gynecological troubles, but also of various metabolic disturbances needing a cautious application of small amounts of estrogen. According to Heilmann (13) the baths provoke a strong dilation of the capillaries combined with a sensation of warmth in the skin. Goldschmiedt (19) discovered that hops *in vitro* increase the consumption of oxygen by the human skin.

So that non-estrogenic material could be eliminated from the wide spectrum of substances contained in hops, two hop extracts, A and B, were studied. The first contained less, the second more bitter acids. As extract B had a higher e.a. in the Allen-Doisy test than extract A, it was decided to try out the e.a. of the bitter acids themselves. For technical reasons we have till now prepared and tested only the β-bitter acid.

Experimental Part

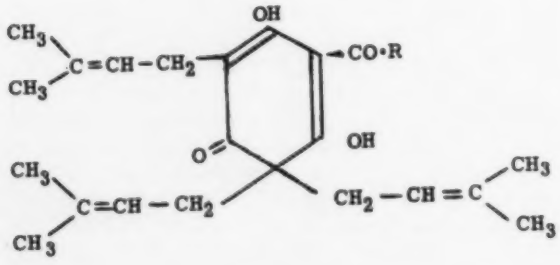
Extract A was prepared by mixing hop extracts with water (containing tannins) and with a lypophile solvent (containing α- β-bitter acids and the respective resins.

Extract B was prepared from an extract of hops with a lipophile solvent (petrol), thus eliminating the hops tannin contained in extract A, decreasing the contents of hard resins, and relatively increasing the bitter acid contents.

Complex β-bitter acids was prepared according to Salac et al. (15) from lupulin (i.e. hop glands filled with a secretion containing bitter acids, resin and essential oils.)

The estrogenic activity was determined by the Allen-Doisy test. Extracts A, B, and the β-acid were administered in olive oil.

β — Bitter acid (synthesized by W. Riedle (20))



— CH $\langle$ CH_3, CH_3 **colupulon**

R — CH_2-CH $\langle$ CH_3, CH_3 **lupulon**

— CH $\langle$ CH_3, CH_2-CH_3 **adlupulon**

Results:

As is evident from the table the highest e.a. is found in the pure β-bitter acid.

	e.a. i.u./gr.	
Extract A	10,000	
Extract B	12,500	
β-bitter acid	15,000	
Hops	300-3,000	
Butea superba[10]	500-900	
Sage[10]	6	
Garlic[10]	4	

Estrogenic activity of β-acid in comparison to certain plants.

Discussion

As already mentioned many plants contain substances with e.a. which, however, is only slight in the majority of cases. Apart from hops and Butea superba, important activity was discovered only in sage and garlic. There is not much known about the substances which cause the e.a. of plants. Apart from the true estrogens (from willow catkins, and palm kernels) the estrogenic principle of the clover Trifolium subterraneum was identified as genistein, and of lucerne as cumestrol.

Our discovery that β-bitter acid has a high e.a. contributes to the identification of a further phytohormone. It is known that this acid is a mixture of four substances. Three of them lupulon, colupulon, and adlupulon have the same structure differing only in the side chain. The fourth, prelupulon, is of an unknown constitution.

Our next task will be to ascertain in what way the four constituents of β-bitter acid contribute to its e.a., and whether also α-acid, which has the same skelett as the components of the β-acid complex is active. Although it cannot, as yet, be demonstrated that the rejuvenating effect of the brewery cold sludge is due to the contents of e.a. substances, our discovery that the β-bitter acid complex has a high e.a. could become the basis for studies of the possible use of hops in cosmetics. Though Jirasek and Trapl (17) discovered that allergic hops dermatitis of hop-pickers is due to lupulin, it is improbable that the β-bitter acid complex itself should be the provoking substance. It would seem that these unfavourable properties are more probably due to the terpenic substances present in lupulin such as limonen, pinen, thuyen, humulen, caryofylen, etc. which are not difficult to remove from the extracts.

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Patent protection in the Soviet Union

The following is reprinted in its entirety from the *Board of Trade Journal* of Great Britain, December 25, 1959 and gives a good picture of the position of foreign owned patents in the Soviet Union at this time.

A United Kindom delegation visited the Soviet Union with the object of discussing with the competent Soviet authorities the protection available in the U.S.S.R. for United Kingdom inventions. The delegation, which left London on November 26 and returned on December 11, consisted of Mr. Gordon Grant, the Comptroller-General of Patents, Mr. William Wallace, Assistant Comptroller of the Industrial Property Department, and Mr. H. R. Mathys, a Fellow of the Chartered Institute of Patent Agents and a Director of Courtaulds Limited. Mr. Mathys was, however, unfortunately forced by indisposition to return to London before the other members of the delegation.

The delegation had most of its discussions with what corresponds in the Soviet Union to the Patent Office, i.e. the Committee on Inventions and Discoveries under the Council of Ministers of the U.S.S.R. It also had talks with the All-Union Chamber of Commerce in Moscow which acts as an intermediary between the foreign owner of an invention and the Committee in the grant of Russian patents and, after grant, notifies the patentee of any interest shown in the Soviet Union in the use of his invention, and with the Ministry of Foreign Trade which has a general responsibility for the licensing in the Soviet Union, of foreign owned patents.

An inventor, Russian or foreign, has, by Soviet law, the option to seek either a patent, which gives him a monopoly in his invention which no one may then use without his permission, or an 'author's certificate.' In the latter case, he assigns his invention to the State which remunerates him according to the amount of use made of his invention and the resultant saving to the economy. Since the latter system involves the inventor in less expense and fits much more aptly into an economic system in which all the means of production are controlled by the State, Soviet inventors invariably seek authors' certificates rather than patents. Foreign owners of inventions, on the other hand, tend to seek patents.

The new Soviet law of April 1959, *so far as it concerns patents*, does not differ in its essentials from the laws of the other countries of the world. There is, of course, in the absence of *contractual* obligations, nothing to stop the copying of foreign inventions in the Soviet Union unless they are patented there. But the Soviet Law, like those of other countries, provides the means whereby, if the necessary steps are taken, inventions can be protected. Before a patent is granted the invention must be described in a specification and a search is made through Soviet and foreign patents and technical literature to make sure that the invention is new. It must also have actual or potential 'industrial utility,' i.e. it must be in a field which, in the opinion of the competent Soviet technical organization, is one in which there is or is likely to be activity. This latter test finds no place in the United Kingdom system which demands instead that the invention be not 'obvious.' If the invention passes these tests a patent is granted and, provided renewal fees are paid each year, the patent lasts for 15 years from the date of application. Subject to the powers reserved to the State to issue compulsory licences (on payment of remuneration to the patentee) 'where an invention is of special importance to the State'—and there is something like this in the laws of most countries it is an offence, during this period, to use the invention without the patentee's consent. The delegation was told that the patentee's monopoly embraces not only the right to prevent others from making goods incorporating the invention but also the right to prevent them from importing such goods.

If a Soviet factory wishes to use an invention the Soviet patent for which is owned by a foreigner, the latter is notified by the Chamber of Commerce. The actual contract is negotiated by the Soviet Ministry of Foreign Trade and one of the import-export corporations. The exact division of responsibility is not clear but there is no doubt that the overall responsibility rests with the Ministry. The delegation

was told of examples of licences negotiated in this way. It is usually sought to make such licences subject to arbitration before the arbitration tribunals of the All-Union Chamber of Commerce in Moscow.

On the question whether or not a patent (or author's certificate) shall be granted, the Committee on Inventions and Discoveries has the final word. The Committee has its own appeals procedures which, the delegates were told, include a right for the inventor to appear and be heard. Disputes as to the *ownership* of inventions are heard by the ordinary courts. If infringement of a patent is suspected, the Committee would, it seems, look into this. In addition, the delegation was told, by the Ministry of Foreign Trade, that infringement actions can be brought before the ordinary courts. It seems reasonable to assume, however, that no such action has ever been brought.

The Soviet officials who received the delegation expressed themselves as anxious to avoid any misunderstanding and the discussions took place in an atmosphere of cordiality and good will. It was clear that the Soviet officials were interested in foreign patent practice, and the delegation got the impression that, so far as the different economic systems permit, were tending to bring their law and practice into line with those followed elsewhere. They seemed interested in the International Convention and had evidently given a good deal of thought to it. The delegation stressed both the practical and presentational advantages of membership of the Convention, and these seemed to be understood. No indication that Soviet membership in the near future was likely, was however given.

Little use has so far been made by United Kingdom owners of inventions of the Soviet Patent system, and there is therefore little practical experience. The language problem and the widely differing concepts of the rights to be enjoyed by the individual as against officials will no doubt lead to some problems. But it seems clear that, at the worst, the owners of worthwhile inventions who contemplate trading with the Russians can only lose the fees they pay, and, from the assurance given to the delegation, may well have a good deal to gain if they patent these inventions in the Soviet Union. In the light of this it seems only reasonable that the Soviet system should be given a fair trial.

The delegation proposes to issue a more detailed report, with a translation of the new Soviet Patent Law at a later date. (*This report is now available through H. M. Stationery Office, Room D. 36, Atlantic House, Holborn Viaduct, London, E. C. 1, England—Ed.*)

The delegation took the opportunity to discuss the protection of trade marks in the Soviet Union. The responsibility for this has recently been transferred to the Committee on Inventions and Discoveries. The system appears not to differ substantially from that in other countries and there is no knowledge of complaint about it. The delegation was told that several hundred British trade marks are registered in the Soviet Union.

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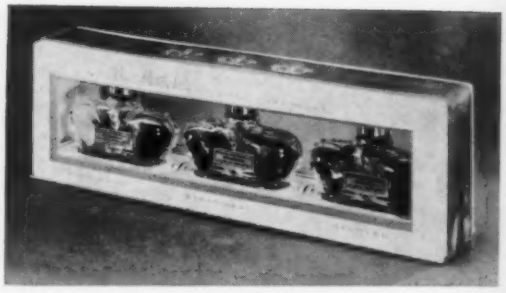

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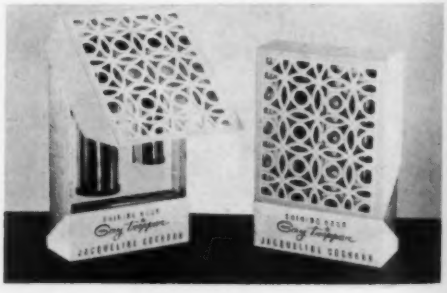

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Futurama Lipstick Box

"Round Cosmetic Boxes"

FIRST AWARD

The Borden Company

Marcelle Dusting Powder

EXCELLENCE AWARDS

ALSO FOR TRANSPARENT BOXES

Prince Matchabelli

Dusting Powder And Cologne Set

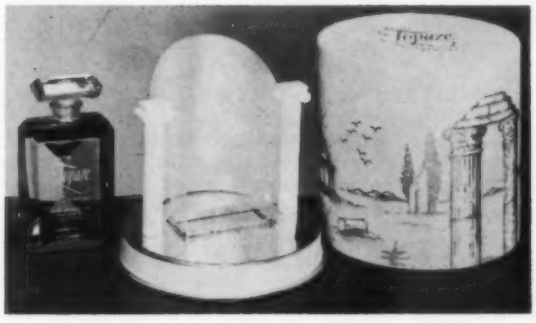
ALSO FOR BEST DISPLAY

Avon Products, Inc.

Avon Topaze Perfume

Elizabeth Arden

Ardena Invisible Veil



"Soap Boxes"

FIRST AWARD

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Soap Box

EXCELLENCE AWARDS

Lora Incorporated

Dogette Shampoo

ALSO BEST SURFACE DESIGN & EXECUTION

Prince Matchabelli

Abano Bath Cosmetics

FDA suggested warnings

The following additions have been made to the list of suggested warnings on drugs and devices for over-the-counter sale by the Secretary of Health, Education and Welfare. This amends Title 21 published in the *Federal Register* of March 26, 1959.

Antiperspirants

Do not apply to broken skin. If a rash develops, discontinue use.

Boric Acid (powdered, crystalline or granular)

Warning—Do not use as a dusting powder, especially on infants, or take internally. Use only as a solution. Do not apply to badly broken or raw skin, or to large areas of the body.

Carbolic Acid (Phenol) preparations (more than 0.5 percent for external use.

Warning—Use according to directions. Do not apply to large areas of the body. If applied to fingers or toes, do not bandage.

Counterirritants and Rubefacients

Caution—Do not apply to irritated skin or if excessive irritation develops. Avoid getting into the eyes or on mucous membranes.

If offered for use in arthritis or rheumatism, in juxtaposition therewith, the statement:

Caution—If pain persists for more than 10 days, or redness is present, or in conditions affecting children under 12 years of age consult a physician immediately.

See also "Salicylates" in this section for additional warnings for preparations containing methyl salicylate.

Dispensers pressurized by gaseous propellants for drugs for external use.

Warning—Keep away from eyes or other mucous membranes. Avoid inhaling.

This warning is not necessary for preparations specifically designed for use on mucous membranes.

Where indicated in order to prevent chilling the tissues, a caution should be included against holding the dispenser too close to the body.

Warning—Contents under pressure. Do not puncture. Do not use or store near heat or open flame. Exposure to temperatures above 130° Fahrenheit may cause bursting. Never throw container into fire or incinerator.

Dressings, protective spray-on type.

Warning—In case of deep or puncture wounds or serious burns consult a physician. If redness, irritation, swelling or pain persists or increases or if infection occurs consult physician. Keep away from eyes or other mucous membranes. Avoid inhaling.

See also dispensers pressurized by gaseous propellants . . . for additional warnings to be included for products under pressure.

Mercury preparations for external use.

Warning—Discontinue use if rash or irritation develops or if conditions for which used persists. Frequent or prolonged use, or application to large areas may cause serious mercury poisoning.

Ammoniated mercury bleach cream:

Warning—Discontinue use if rash or irritation develops. Do not apply to irritated or damaged skin (cuts, bruises, sunburn) or after shaving or using a depilatory. Do not apply to children under 12 years of age.

Resorcinol (not the Monoacetate) hair preparations

Caution—Excessive use of this preparation may temporarily discolor blond, white, or red hair.

Salicylates: methyl salicylate (wintergreen oil).

Warning—Do not use otherwise than directed. Keep out of the reach of children to avoid accidental poisoning.

If the preparation is a counterirritant or rubefacient the statement:

Caution—Discontinue use if excessive irritation of the skin develops. Avoid getting into the eyes or on mucous membranes.

If offered for use in arthritis or rheumatism, in juxtaposition therewith, the statement:

Caution—If pain persists for more than 10 days, or redness is present, or in conditions affecting children under 12 years of age consult a physician immediately.

Silver

Caution—Frequent or prolonged use of this preparation may result in permanent discoloration of skin and mucous membranes.

Sodium perborate mouth wash and gargle and toothpaste

Caution—Discontinue use if irritation or inflammation develops, or increases. Avoid swallowing.

Sulfur preparation for external use

Caution—If undue skin irritation develops or increases, discontinue use and consult physician.

Zinc stearate dusting powders

Warning—Keep out of the reach of infants and children; avoid inhaling.

Alcohol rubbing compound

Warning—For external use only. If taken internally serious gastric disturbances will result.

Antibiotic-containing drugs for external use for prevention of infection

Caution—If redness, irritation, swelling, or pain persists or increases or if infection occurs, discontinue use and consult physician. Do not use in the eyes.

Bacitracin-containing ointments

For use only in the prevention of infection in minor cuts and abrasions.

Use of the drug should be discontinued and a physician consulted if signs of infections or irritation appear.

Bacitracin (zinc bacitracin)—polymyxin ointment; bacitracin-polymyxin-neomycin ointment

For use only in the prevention of infection in minor cuts and abrasions. Use of the drug should be discontinued and a physician consulted if signs of infection or irritation appear.

If it is in liquid form, also the statement "Not for injection."

Sodium fluoride dentifrice powder

Caution—Children under six years of age should not use this drug.

Sodium monofluorophaste dentifrice solution

Caution—Children under six years of age should not use this drug.

Technical digests

Average Growth Predicted for Chemical Industry in 1960

(digested from CHEMISTRY IN CANADA, January, 1960, Vol. 12, No. 1 p. 36)

The chemical industry went on to establish new records in 1959, but its rate of growth fell far behind its long term record. It had been forecasted that 1959 would be a better than average year. Mr. Fleming, the Finance Minister, estimated that the Gross National Production would rise by some 7% to reach a figure of about $34.5 billion and that prices would remain relatively stable throughout the year. It now appears that when the final figures are in for 1959 they will look very much like the figures that were forecast in the Budget of last April. There was a rapid resurgence of growth in the early part of the year that leveled out, and remained on a plateau until late in the year. This leveling out action can be explained in two ways. First of all, it is typical of the recovery phase of most business cycles to experience this circumstance, and secondly, it can be surmised that the U. S. steel strike had some impact upon business expansion in Canada. There were few new business opportunities last year and private business was just getting over the building boom of 1955-1957. But the average consumer was spending more, the governments were spending more, and there was spending by business for inventory accumulation.

For the year the production of chemicals and allied products rose by 2% over 1958. There has been a rising level of profits with the total profits reaching $56 million. There appears to have been a slightly more upward price pressure in the chemicals sector than there was for the economy as a whole. There was no pronounced price pressure in any of the individual chemical lines. Manufacturers' shipments of medicinals and pharmaceuticals, soaps and washing compounds, and toilet preparations all rose by 7 or 8% last year. The acid, alkali, and salt group showed a gain of at least 10% in manufacturers' sales. The largest gain of all was the 15% recorded by the adhesives industry. Thus, all sectors with the exception of fertilizers and synthetic rubber experienced above average growth rates.

The year 1960 looks like a year of average growth and one in which most sectors of the economy will forge ahead. Personal consumption and government expenditures are again expected to rise although the latter should not go up by the same degree as they have in recent years. New growth is expected in those two sectors that did not contribute much to growth last year, namely export trade and capital investment. It is concluded that Gross National Product should grow by about 5% this year, and on this basis, chemical consumption in Canada should rise by about 5%. In 1960 the total market for chemicals in Canada should exceed for the first time the $1.5 billion a year level. Even though cost problems and import competition will still be of some concern to the chemical industry, there should be a phenomenal expansion over the next ten years.

A Comparative Study of Pharmaceutical Emulsification Equipment

By Garnet E. Peck, H. George Dekay, and Gilbert S. Banker.

A paper by Peck, Dekay, and Banker, which dealt with the study of six common types of emulsification equipment, appeared in the February, 1960 issue of the JOURNAL OF THE AMERICAN PHARMACEUTICAL ASSOCIATION.* This equipment was used to prepare various emulsion samples which were observed for their degree of creaming, apparent viscosity, and the particle size distribution of the dispersed phase. The equipment used is represented by the following table:

	rpm	setting
Agitators		
Wall mixer	1,700	
Waring Blender	10,000	
Eppenbach Homo-mixer	1,700 and 7,000	
Colloid Mills		
Tri-Homo dispenser	7,000	
Eppenbach	7,000	
Homogenizer		
Manton Gaulin		3,000 and 8,000 p.s.i.

The emulsions used were the official liquid petrolatum emulsion N.F.X., cod liver oil, liquid petrolatum and Tween 80 and Arlacel 80, and a liquid petrolatum emulsion using the USP method. For the first three emulsions the general procedure consisted of mixing the oil and emulsifying agent together for one minute at 1,000 rpm, adding the proper volume of water all at once, adding the remaining ingredients, and mixing at 1,7000 rpm for 5 minutes. All the equipment was standardized for use; the temperatures were observed carefully; and all viscosities checked twenty-four hours and one and two months after preparation with the Brookfield viscometer (MODEL RVF). Samples were observed in calibrated tubes and the degree of separation was recorded by the measurement of the aqueous layer. The results were plotted against time. The particles size was measured on 400 globules of each emulsion by means of a standard microscope and photomicrographs. It was shown that there was a definite increase in the member of globules per unit area as the size of the globules was reduced. It was also observed that an emulsion temperature increase occurred with all the equipment, especially with the Eppenbach Homo Mixer that showed an increase of 20°. Emulsions prepared with acacia were more viscous than either the gelatin or Tween-Arlacel combination type. The Manton Gaulin Homogenizer at 8,000 p.s.i., which produced a smaller average particle size and the least amount of creaming, was generally the most effective of all the equipment studied. An analysis of variance of the mean particle size data indicated that significant differences existed between the three emulsifying agents, the six pieces of equipment, and the interaction between the emulsifying agents and equipment should be carefully studied.

**Vol. 49, No. 2. p. 75.*

Antifungal Action of Salicylanilide II

There is a definite need for a study explaining the mode of antifungal action of salicylanilide and compounds related to it since data relating to the structural specificity essential for the biological activity exhibited by this agent is lacking. Baichwal, Baxter, Kandel, and Walker undertook a study of this nature in the 38th volume of the CANADIAN JOURNAL OF BIOCHEMISTRY AND

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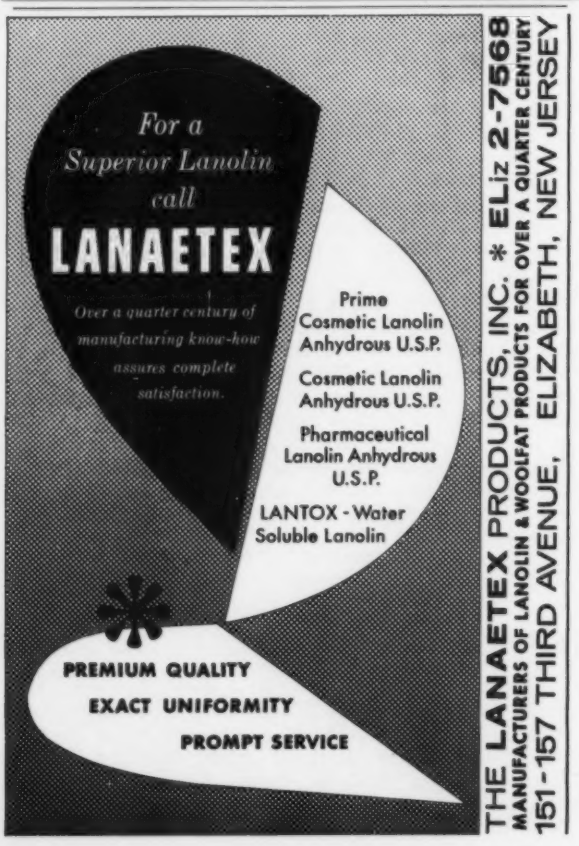
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PHYSIOLOGY, Number 3, March, 1960.* The organism used in this study was Trichophyton Mentagrophytes 183. The media used was one of 2% glucose and 1% bactopeptone, and a broth media solidified with 2.5% Difco agar. For the determination of the fungistatic activities of the test compounds, the tube dilution method was followed. The pK_a values of salicylanilide and its chloro derivatives were determined potentiometrically by the method of Stockton and Johnson. The reactions with specific reagents, such as Janus green B and cobalt nitrate, were studied using agar medium, the test organism, and standard cylinders of salicylanilide solution in order to determine if inhibition of certain types of enzymes occurred in the presence of salicylanilide. The plates were incubated and the zones of inhibition closely observed. The plates were flooded with the specific reagents and the color changes were noted. These color reactions are based on an effect on oxidizing and reducing systems involved in aerobic respiration.

It can be seen that with the exception of the chloro derivatives, all the other compounds tested were not as active as salicylanilide. The removal of the hydroxyl group, or the blocking of this hydroxyl group with a methyl group, or the substitution with a carboxyl or a sulphydryl group, reduces the activity of the parent compound. The amide group appears to be of great importance for activity. The decreased activity of phenyl salicylate and salicylic acid indicates the importance of the anilide group. It was shown that a potentiality for chelation with the phenolic and the amidic oxygen atoms is recognized for salicylanilide. It is suggested by Chaplin and Hunter that the association found in salicylanilide is due to the formation of a hydrogen bond between the anilide H atom of one molecule and an electron donor atom of the other. Three possible ways in which a bridge formation may occur are:

(a) to the amide N atom,
(b) to the phenol O atom, (phenolic),
(c) to the amide O atom, (amidic).

It is conceivable, then, that the hydrogen bond formation by the anilide H atom of the molecule might well take place with an electron doner atom of a polypeptide or an enzyme of the organism. The bonding might take place with the amidic oxygen of a peptide of a vital enzyme system. The increased activity of the salicylanilide molecule on substitution of halogen atoms in suitable positions might be explained on the basis of the mesomeric effect of such groups on the hydrogen bonding capacity and/or the chelating ability of the new molecules. The pK_a values were determined, and it was shown that the fungistatic activities increase as the pK_a values decrease.

The inhibition of enzymes was followed through the development of color reactions on assay plates. The reagents used, which are considered to be specific for -SH groups in living cells and tissues, failed to indicate the presence of these groups in the zones of inhibition. They did appear, however, on the outside of these zones where normal growth of the organism appeared. At least four of the reagents showed intensified boundaries between the areas of inhibition and normal growth. Thus, tests or the influence of subinhibitory concentrations were carried out, and it was determined that there was a stimulation of growth in their presence. There was a decreased activity in zones of inhibition with the other reagents. The reactions of the last few reagents used in these experiments indicate that the mode of action of salicylanilide may be related to enzymes containing sulphydryl groups.

*p. 245.

New PRODUCTS & IDEAS

Quick breaking foam latest in aerosol developments

A new foam that immediately breaks into liquid when disturbed or warmed by body heat is finding applications in aerosol packaging of nail polish remover, after shave lotion, and hair dressing preparations. The basic formulation of the new aerosol foam is:

Ethyl Alcohol	46.0-66.0%
Surfactant	0.5-5.0%
Water	28.0-42.0%
Propellant	3.0-15.0%

The proportion of surfactant is between 1/2 and 1/20 of that used in formulations for regular-foam products, such as aerosol shave cream. Surfactant can be nonionic, anionic or cationic but should be soluble in only one of the miscible solvents. In all cases the aerosol should be filled while the concentrate is warm. **Allied Chemical's General Chemical Division.**

Can and bottle cap has built-in "gasket"

A low-cost cap made of Marlex linear polyethylene has been designed to eliminate the traditional liner. A built-in "gasket" as part of the basic cap serves as a sealing band. The cap eliminates the problem of liners sticking to spouts or lost seals which cause leakage. It is priced competitively with metal screw caps. **Dover Molded Products Co.**

Polyethylene and plastic scented by new process

Poly-Scent is an additive which now makes it possible to impregnate polyethylene film and plastic products with lasting aromas. The additive is incorporated into film by the extruder and into plastic products by the injection molder. **Fragrance Process Company, Inc.**

Illustrating a new and improved revolving plastic cap produced by G. Felsenthal & Sons, Inc., subsidiary of J. L. Clark Mfg. Co., Rockford, Ill.

Revolving plastic cap

A snug-fitting revolving plastic cap for talcum powder cans and similar uses was introduced at the A.M.A. National Packaging Exposition. Designed of polyethylene it compares favorably in cost with both revolving metal caps and plastic slip caps now in use. The cap turns at the gentlest touch and stops for open and closed positions are provided, with sift-proof contents protection assured. **J. L. Clark Manufacturing Company.**

"King size" stirrer for laboratory vessels

A unit has been designed to fill the needs for laboratory stirring of larger vessels where controlled heat is a factor. Made of heavy steel the unit has an eight inch square hot plate of solid aluminum, with a fully enclosed heater of 1,000 watt capacity. Accurate temperature is maintained by a built-in adjustable thermostat. The stirrer and hot plate operate independently with separate controls for the stirrer motor. The unit, called "Pyro-Magnestir", is especially effective for both open or closed vessels using glass or Teflon-covered bars. **Labline, Inc.**

Iodophors—Iodophors in Dermatology, Burdick, K. H., A.M.A. Arch. Derm. 80:587 (Nov.) 1959

A new type of detergent-iodine complex of the "iodophor" group was used in treating primarily or secondarily infected skin diseases for a four-year period and was found to be effective over a wide range of infectious agents. The iodophor evaluated had the following composition:

Polyethoxy polypropoxy ethanol-iodine complex Nonylphenyl ether of polyethylene glycol-iodine complex	7.75%
Hydrogen chloride	0.10%
Inert material	84.40%

This detergent-iodine complex was found to have the following advantages over its older counterparts: (1) When properly used, it was found to be relatively free from toxicity, irritation, staining and odor. (2) It penetrated rapidly into fatty materials and was not rapidly bound to proteins. (3) It was stable under normal storage conditions and was water soluble. The following tabulation summarizes the clinical impression of this compound:

Excellent Results: (one-ounce-to-one-liter dilution)
- Kaposi's varicelliform eruption
- Secondary impetiginized dermatoses
- Mixed intertriginous infections
- Infectious eczematoid dermatitis
- Molluscum contagiosum

Very Good Results: (one-ounce-to-one-liter dilution)
- Herpes zoster
- Folliculitis
- Hidroadenitis suppurativa
- Dermatophytosis
- Monilial paronychias (Applied full strength)
- Onychomycosis (Applied full strength)
- Flat or juvenile warts (Applied full strength)

Satisfactory Results (one-ounce-to-one-liter dilution)
- Pustular bacteria
- Dermatitis repens
- Furunculosis

Robert L. Ravin
Thru Am. J. of Hospital Pharmacy, 17, 3, 190(1960)

The Significance of Enzymes in Seawater— Henry Goldschmeidt

My research project started from the fact that no fishbones and crustacean shells can be found at the bottom of the sea in spite of the fact that such materials are constantly being discarded. Since these substances consist mainly of water-unsoluble tribasic calcium phosphate, I was looking for a "solvent". My research showed that enzymes, especially alkaline phosphatase, convert the tribasic calcium phosphate into water-soluble monobasic or dibasic calcium phosphate.

These findings are of great importance because whereever there is dissolution of bonematter in the human body (caries, periodontal disease, bone diseases) I have found that there is a definite increase in alkaline phosphatase. I further was able to show that the beneficial effects of sodium fluoride are obviously due to the fact that it is an inhibitor of alkaline phosphatase. *Thru Chem. Ztg. Chem. Appt. 83, 442 (1959)*

Improved Hydrogen Peroxide—Treatment of Pharyngitis and Laryngitis with an Improved Hydrogen Peroxide, Harkins, H. P., Eye, Ear, Nose, Throat Monthly 88:942 (Nov.) 1959.

Because of the increasing incidence of bacterial resistance and allergy to antibiotics, long established antibacterial agents are being re-evaluated for their usefulness in the treatment of tropical diseases. As a result, hydrogen peroxide has been reconsidered for the following reasons: (1) It is a wide spectrum bactericide and is effective against some fungi. (2) It is nonallergenic, completely nontoxic, nonirritating and nonsensitizing. The main disadvantage of the 3% aqueous solution of hydrogen peroxide is that it is very rapidly broken down by the catalase present in most body fluids so that its action is fleeting. However, it was found that a product (Gly-Oxide G.H.P.) containing 10% urea peroxide in glycerin remains stable and releases hydrogen peroxide over a long period of time when in contact with pharyngeal and laryngeal mucosa. This product was found to have special debriding and detergent action and was most effective in relieving the itching and burning which accompanies smoker's pharyngitis. Robert L. Ravin. *Thru Am. J. of Hospital Pharmacy, 17, 3, 190 (1960)*

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Trade Literature

Proceedings of the CSMA

• The proceedings of the 45th mid-year meeting of the Chemical Specialties Manufacturers Association have been published and are available from the Association at 50 East 41st Street, New York 17, New York. The 204-page book consists of all papers, discussions and committee reports from the May 18-20, 1959 meetings which were held in Chicago. Prices are $7.50, postpaid in the United States and Canada, and $8.00, postpaid to other countries.

Surfactants Data

• A new 44-page booklet, describing the properties and uses of Tergitol surfactants, has been published by Union Carbide Chemicals Company, 30 East 42nd Street, New York 17, New York. The booklet contains extensive data for eight nonionic and four anionic surfactants, including selection, solubilities, properties, formulations, applications, performances, specifications and test methods, shipping, bulk storage, and physilogical properties. A detailed bibliography and reference section is included. Both types of surfactants give rapid wetting and penetrating action, but under different conditions. The nonionic surface active agents are of the polyethylene glycol-ether type, while the anionic surface active agents are basically sodium salts.

Cosmetic Cream Formulary

• A formulary for cosmetic creams and lotions is available from Cosmetic Department, Gum & Technical Products Division, Morningstar-Paisley, Inc., 630 West 51st St., New York 19, New York. It is an eight page folder containing specific formulas for twenty-one products, including all-purpose, cleansing, hair, hand hormone lubricaing, moisturing, night, and vanishing creams. All formulas incorporate absorption bases, versatile modern oil-in-water and water-in-oil emulsions that have revolutionized the cosmetic industry.

Laboratory Specialties

• A fully illusrated forty-eight page catalog of laboratory specialties is available from Fisher Scientific Company, 318 Fisher Building, Pittsburgh 19, Pennsylvania. It describes many instruments ,appliances and other laboratory equipment designed in the Fisher Development Laboratories and not available elsewhere, as well as apparatus Fisher distributes exclusively.

Aluminum Aerosols

• An eight-page catalogue on aluminum aerosol containers is available from Peerless Tube Company, 58 Locust Avenue, Bloomfield, New Jersey. These are four-ounce content and under containers of extruded, one-piece, seamless construction. The catalogue lists the 10 sizes, ranging from one-half to four fluid ounces, and describes the inside resin coatings and exterior finishes available. Decorated containers are produced in one to four-color lithography over a base coat and can be further coated with a highly resistant lacquer for protection against alkalies or acids.

Super-speed Centrifuges

• A new 16-page illustrated catalog announcing thirteen improved models of super-speed centrifuges has been published by Lourdes Instrument Corporation, 53rd Street and 1st Avenue, Brooklyn 3, New York. All models come equipped with built-in, automatic self-centering devices, with relative centrifugal forces up to 27,000 x G. Roters have capacities up to 3,000 ml and speeds up to 18,000 rpm's. Both automatic and non-automatic models come equipped with or without acceleration and deceleration. Included in the new series of continuous-flow centrifuges are rotors which have removable polyethylene liners for readily collecting sediment while liquid is continuously ejected. Automatic rotor acceleration may be pre-set to any desired speed.

Ketones

• A new 48-page booklet describing ketones as solvents and chemical intermediates has been published by Union Carbide Chemicals Company, 30 East 42nd Street, New York 17, New York. The booklet has data on fifteen ketones and diketones that are available in commercial quantities from Carbide. It includes information on applications, coatings, formulations, physical properties, solvent properties, constant-boiling mixtures, shipping, storage, handling, physiological properties, specification limits, and test methods. A comprehensive bibliography on ketones and their uses is a feature of the new publication.

Silicone Products

• A guide to a line of silicone products is available from General Electric, Silicone Products Department, Waterford, New York. Listing major product uses and benefits, this publication features silicones for: antifoam and release agents, lubricants, paper release, cosmetics and polishes.

Polyethylene Glycols

• A new forty page booklet describing Carbowax polyethylene glycols for use in pharmaceuticals and cosmetics has been published by Union Carbide Chemicals Company, 30 East 42nd Street, New York 17, N. Y. The booklet contains data on polyethylene glycols ranging in molecular weights from 200 through 600, on physical and physiological properties ,solubilities, aqueous solution viscosities, surface tensions, and phase diagrams, hygroscopicity, and viscosities of polyethylene glycol blends. It provides preparation and formulation instructions for ointment and suppository bases, cosmetic preparations, parenteral solutions and histological and pathological preparations.

Sanitizing Products

• A technical bulletin describing the formulation of household sanitizing products is available from R. T. Vanderbilt Company, 230 Park Avenue, New York 17, New York. This bulletin contains a general discussion of sanitizing products, nine formulas for household sanitizing products and bacteriological test data on these formulas and discussion of results.

Surfactant Catalog

• A new twenty-four page catalog of surface active agents has been published by the Onyx Oil & Chemical Co., Jersey City 2, N. J. Each product is described by trade name, active ingredients, percent activity, physical state, general use, specific applications and properties. The products are divided into three general classes: anionic, cationic and non-ionic. There is a two page section explaining the chemistry of each of these groups.

Price Lists

• Haarmann & Reimer, 20b Holzminden, Weser, Germany. Aromatics. Dated February/March 1960.

Pylam Products Company, Inc., 799 Greenwich Street, New York 14, New York. Certified colors. #C-L.

Verona Aromatics, 26 Verona Avenue, Newark 4, New Jersey. Aromatics. Dated 1960.

Fritzsche Brothers, Inc., 76 Ninth Avenue, New York 11, New York. Essential oils, aromatic chemicals, and other perfumery materials. Dated March, 1960.

. . NEWS AND EVENTS . . . NEWS AND

FTC chairman addresses Cosmetic Career Women luncheon

Earl W. Kintner, chairman of the Federal Trade Commission spoke before a luncheon of the Cosmetic Career Women in New York City on April 19th on the subject "Truth in cosmetic advertising". Mr. Kintner said in part ". . . if the creative ability of those who develop advertising gambits and who are, I understand, rather handsomely remunerated for it is of the genius variety we are led to believe, they should have no difficulty in reconciling their imaginative fantasy with legality of phraseology. Nor should it prove so unnerving to learn when and where their efforts have exceeded those limits."

New cosmetic line to debut in fall

A line of medium-price makeup and hair items will be introduced this fall by Dorothy Lamour, Inc. The products will be marketed in the company's own salons which will be located in New York and northern New Jersey. Plans are in progress for additional salons to be opened in Chicago, Boston, Philadelphia and Washington. Miss Dorothy Lamour, of movie fame, will be executive director and a member of the executive committee taking part in all of the company's operations. Mr. George Alpert, formerly head of his own merchandising and consulting company in New York City, is president of the firm.

. Dias guests at Cosmetic Career Women's sixth annual Men's Day luncheon. (left to right) The Honorable Lowell B. Mason, former member Federal Trade Commission, Miss Dorothy Fay, executive director, U. S. Trademark Association, H. W. Hamilton, executive vice-president, Chemical Specialties Manufacturers' Association, Miss Helen L. Booth, secretary, Drug, Chemical and Allied Trade Association, The Honorable Earl W. Kintner, chairman, Federal Trade Commission, Miss Gina Kohrman, J. Walter Thompson Company, chairman of the luncheon, S. L. Mayham, executive vice-president, Toilet Goods Association, and Lee H. Bristol, Sr., chairman, Advertising Council, Inc. and chairman of the board of Bristol-Myers Company.

Study of beauty product buying available from Dell Publishing

The Dell Modern Group of romance and screen magazines has completed its 21st survey of women's preferences in buying ninety-one types of beauty products. A booklet covering 1959 brand usage according to purchasers' yearly income, location by city size, and places where products were bought, together with data for the 1940 to 1959 period including yearly tabulations of percent usage, median prices paid, purchases by price class intervals and usage by age groups is available from the Market Research Department, Dell Publishing Co., Inc., 750 Third Avenue, New York 17, New York. The survey is classified in product categories of face make-up, eye make-up, skin care, hair care, hand care, mouth care, body hygiene and fragrances. Anyone desiring results of the survey should specify the product category in which he is interested.

Colgate-Palmolive re-elects fifteen directors

The stockholders' meeting of Colgate-Palmolive Company resulted in the re-election of fifteen directors plus the election of John L. Bricker as a director replacing Stuart Sherman who withdrew from active business last year because of ill health. The board of directors re-elected Edward H. Little chairman of the board and chief executive officer and elected George H. Lesch president of the company. All other officers were re-elected.

Helene Curtis reports highest earnings in its history

Helene Curtis Industries, Inc. ended its fiscal year with the highest earnings recorded in the company's history. Net profit on sales of $48,058,616 was $2,489,803.

In attendance at St. John's University Aerosol Technology Seminar are (left to right): David Tillotson, Isotron Propellant Technical Services, Pennsalt Chemical Corp.; Dr. Samuel Livengood, assistant director, Union Carbide Chemicals Co. Technical Serivce Laboratory; Dr. Fred Reed, head of the aerosol division, Freon Products Laboratory, E. I. DuPont de Nemours; Dr. John J. Sciarra, associate professor of pharmaceutical chemistry, St. John's; Lloyd Flanner, head of the technical service laboratory of the General Chemical Division of the Allied Chemical Corp.

deNavarre receives Alumni Award from Wayne State University

Maison G. deNavarre, editorial director of *American Perfumer* and vice president and director of Cosmetic Laboratories, Inc., received an Alumni Award at Wayne State University's 92nd Alumni Reunion on May 14th at Detroit's Sheraton-Cadillac Hotel. Mr. deNavarre received his Bachelor of Science degree from the University in 1930 and his M.A. in 1957.

Packaging Institute holds aerosol technology seminar

Professional members of the Packaging Institute will hear an eighteen man panel answer questions on the technology of aerosol packaging at a special seminar on June 1 at the Statler-Hilton Hotel, New York City. Members of the panel are Jean W. Baer, Sprapak Chemicals, Inc.; Charles E. Beach, Stalfort Pressure-Pak, Inc.; John Beacher, Avon Products, Inc.; Walter C. Beard, Risdon Manufacturing Co.; L. G. Cannella, Continental Can Co.; Victor Di Giacomo, Givaudan-Delawanna, Inc.; J. J. Gregory, Newman-Green, Inc.; A. R. Marks, Wheaton Plasti-Cote Co.; Russell McGhie, Colgate-Palmolive Co.

Also, Dr. Francis A. Mina, Reed Camrick Co.; Ralph Minerrino, Metal Fabricating, Inc.; John J. Palmer, Peerless Tube Co.; H. E. Peterson, Peterson Filling and Packaging Co.; Joseph Pizzurra, Precision Valve Co.; W. M. Robertson, Owens-Illinois Glass Co.; H. R. Shepherd, Aerosol Techniques, Inc.; Ralph Thomas, Bristol-Myers Co. and Sigmund Was, Emson Research, Inc.

Panel moderator will be Fred T. Pickerell of the Schering Corporation.

Shulton to build new plant

Shulton, Inc. has announced plans to build a 111,000 square foot building on a twelve acre site in Belz Industrial Park, Memphis, Tennessee. Mr. John Kitson, production manager of Shulton's Clifton, New Jersey plant, has been named plant manager. Operations of the combination warehouse and production facility are expected to begin in the fall. Initial employment at this plant will be fifty people.

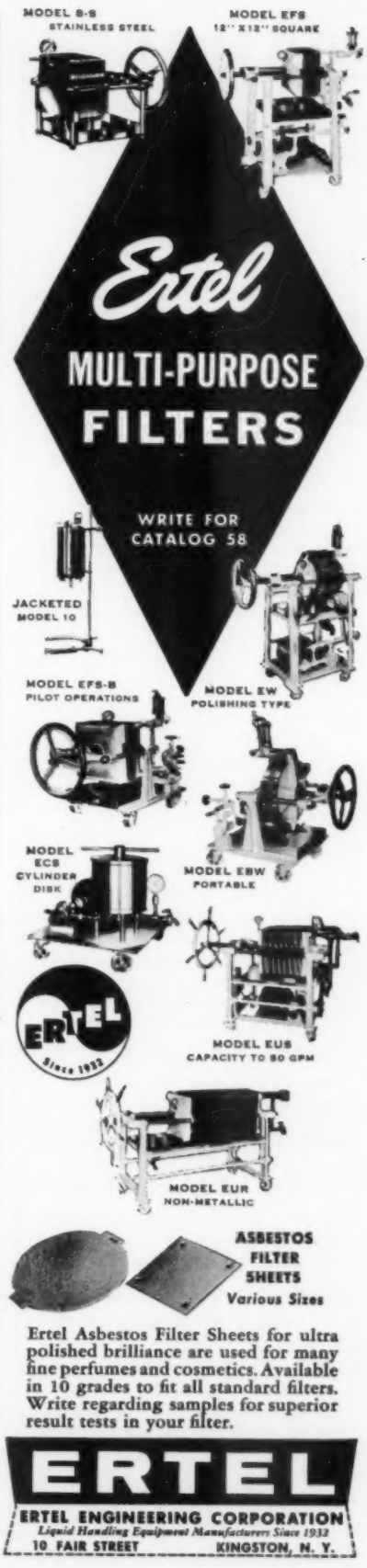
Malmstrom Chemical cited for safety

The Malmstrom Chemical Corp., Newark, New Jersey, has been awarded a "Citation of Merit" in the 32nd New Jersey State Annual Safety Contest. The award was made "for working throughout the year 1959 without suffering a disabling injury." Presentation was made at a dinner co-sponsored by the State Department of Labor and the State Industrial Safety Committee.

Breck Company honored for employing physically handicapped

John H. Breck, Inc., Springfield, Massachusetts, was appointed to an organizational membership on President Eisenhower's Committee for the Employment of the Physically Handicapped and at the same time a citation for outstanding service to the handicapped was presented to John H. Breck, Sr., founder and chairman of the board of the company.

Membership on the committee is an honor given in recognition of a company's interest in the employment of the handicapped.



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Obituary

Dr. Paul Langlais, technical director of Charabot & Cie., died on March 30 in Grasse, France. For the past 22 years Dr. Langlais served Charabot's research laboratories and has written numerous articles and papers on a number of subjects pertaining to the perfume industry.

Great Britain SCC hears paper by E. S. Maurer

E. S. Maurer, who was recently awarded Honorary Membership in the American Society of Perfumers, delivered a paper on "Fragrance in the Natural Orders" before the March 15th meeting of the Society of Cosmetic Chemists of Great Britain.

New SCC chapter established

A group of 48 New England chemists has received a charter to become the fourth United States chapter of The Society of Cosmetic Chemists. Officers elected for 1960 are Dr. Richard Faust, Cuticura Labs, chairman-elect, Myron Slotsky, Gillette Safety Razor Co., secretary, Jesse H. Starkman, Gillette Safety Razor Co., chairman, and Donald Kirby, John H. Breck, Inc., treasurer.

The new chapter plans to hold meetings in Boston on the fourth Thursday of each month. Those interested in joining may contact the secretary, Myron Slotsky, Gillette Safety Razor Co., Gillette Park, South Boston, Massachusetts.

Netherlands firm exporting cologne to U. S.

J. C. Boldoot Company is introducing its cologne and buttermilk soap in this country through Mimi Hellinger, P. O. Box 514, East Chester Street, Long Beach, New York, exclusive U. S. importer. The Amsterdam firm has an extensive line of beauty products and toilet goods some of which they intend to add to their list of exports together with some new products which are now in the experimental stage.

Aerosol Techniques executive makes a good guess

David Benjamin, assistant to the president of Aerosol Techniques, won a gift certificate and a slide rule for making the closest guess on the quantity of polypropylene film required to wrap Atlantic City's Convention Hall site of the American Management Association's packaging show. Mr. Benjamin computated the quantity within .4000 of an inch.

Owens-Illinois buys interest in Brazilian firm

Owens-Illinois Glass Company has purchased a minority interest in one of Brazil's leading glass container companies, Companhia Industrial Sao Paulo E Rio, popularly known as Cisper. A technical assistance and patent license agreement has been signed with this company which is the only glass container manufacturing company in Brazil with plants in both Rio de Janeiro and Sao Paulo.

Officers and committee chairman for 1960 of the New England Chapter of The Society of Cosmetic Chemists are standing (left to right) R. Reavey, John H. Breck, Inc., Legislative Committee, Dr. E. Levy, Gillette, Inter-professional Committee, H. Harris, S. B. Penick, Membership Committee, J. Akerson, Gillette, House Committee, J. Dugan, Dodge & Olcott, Special Events Committee, and R. Swaine, A. D. Little, Publicity Committee.
Seated (left to right) are Dr. Richard Faust, Cuticura, Chairman-elect, Myron Slotsky, Gillette, secretary, Jesse Starkman, Gillette, chairman, and Donald Kirby, John H. Breck, Inc., treasurer.

In attendance at the April luncheon of Cosmetic Industry Buyers & Suppliers Association were (left to right) James E. Boyer, Lehn & Fink, Lamson Scovill, Scovill Manufacturing Co., president of CIBSA, Charles T. Lipscomb, Jr., president of the Bureau of Advertising of the American Newspaper Publishers Association, who addressed the group on "Keys for Successful Business Operation", Dallas D. Roush, Owens-Illinois Glass Co., and Horatio R. Rogers, Jr., Colgate-Palmolive Co.

Cosmetic marketed exclusively in grocery stores

Capri Cosmetics, Memphis, Tennessee, is marketing their line of shampoo, lipstick, rouge, face powder, eye shadow, and lotions exclusively in grocery stores. Both chain and independent grocers in the Memphis area are carrying Capri Cosmetics in special displays in keeping with the company's "Isle of Beauty" theme. Capri products are manufactured by several different firms but the company hopes to eventually take over all bottling and packaging sometime in the future.

Newspaperwoman to speak to Chicago SCC Ladies Night

Norma Lee Browning of the *Chicago Tribune* will address the Chicago Chapter of the Society of Cosmetic Chemists Annual Ladies' Night on Tuesday, June 14th. Miss Browning who won an A. S. Beck Award for her series of articles exposing quack doctors, will speak on "So Who Wants To Grow Old." The meeting will be held in Henrici's Restaurant in the Merchandise Mart beginning at 6:00 P.M.

Meeting notice

The Society of Pharmacists in Industry will hold its meeting on Monday, May 23rd at the Academy of Science in New York City. Marc Woodward, executive director of Health News Institute will speak to the group on research, competition and profits. This is an open meeting to which guests are invited.

Oscar Mayer aerosol subsidiary expands operations

The Kartridg Pak Co. of Franklin Park, Illinois, subsidiary of Oscar Mayer & Co., has purchased Alpha Engineering Works, Inc., Mt. Prospect, Illinois, a contract engineering firm and a pioneer in the development of aerosol filling equipment. The acquisition is intended to strengthen the engineering and research facilities at Kartridg Pak, as well as increasing the manufacturing volume. The company will become a division of Kartridg Pak operating under the name of Alpha Engineering Service.

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PERSONALITIES

Edmund Kowalczyk

Edmund Kowalczyk has joined Helene Curtis Industries, Inc. as director of industrial relations. Mr. Kowalczyk was formerly with Ethicon, Inc., a Johnson & Johnson affiliate, in a similar capacity.

Norbert A. Witt will fill the newly established office of executive vice president at Noxzema Chemical Company. **Leo D. Dunham** was named vice president and sales manager and **J. Edward Fry** was appointed assistant to the sales manager.

Mr. Witt has been with Noxzema since 1955 as vice president in charge of sales.

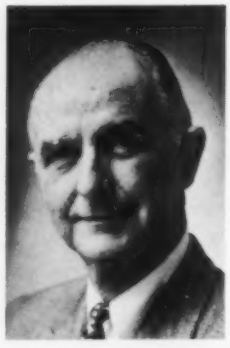
Mr. Dunham, formerly assistant sales manager, joined the company in 1949.

Mr. Fry came to Noxzema from Bristol-Myers Company and previous to this appointment he was midwest sales representative for the company.

Matthew J. Middleton

Joseph J. Galietto is the new general sales manager of the Hudnut-DuBarry Division, Warner-Lambert Pharmaceutical Company. He will be responsible for the sales force of the Hudnut, DuBarry and Sportsman lines of cosmetics and toiletries. Mr. Galietto was previously with the Knomark Division of Revlon as general sales manager.

Edward P. Field, Jr., general manager of Colgate-Palmolive Company's Associated Products Division, has been named a vice president of the company. Mr. Field joined Colgate-Palmolive in 1952 and became general manager of the Associated Products Division in 1957.



Frank J. Woods

Frank J. Woods has been appointed director of sales for Allied Chemical's General Chemical Division. Mr. Woods has been with the division for twenty-two years and has been heavy chemical sales manager for the past ten years.

Matthew J. Middleton has been named vice president of Hazel Bishop, Inc. and **Kenneth M. Freedman** has been appointed sales manager of the company.

Mr. Middleton joins Hazel Bishop following a year of consultative work, prior to which he was director of marketing for Helena Rubinstein, Inc.

Mr. Freedman was formerly general sales manager of the Lady Esther division of Chemway Corporation.

Theodore A. Thonet has been named associate research director of Puritan Aerosol Corporation, private label and custom loader of aerosols for the pharmaceutical, cosmetic and

Theodore Thonet

chemical specialties industries. Mr. Thonet was formerly associated with Continental Filling Corp. and is the author of an article appearing in a recent issue of *Aerosol Age* on gas chromotography in the aerosol laboratory.

Lee Henderson is now representing Bourjois, Inc. in the Michigan, Ohio and Indiana area. Mr. Henderson most recently was with Shulton, Inc. and served for four years in the Detroit area for this company.

Kenneth M. Freedman

Eldridge J. Black

Eldridge J. Black has been named vice president and general manager of Stepan Chemical Company's newly-formed Industrial Chemicals Division. **Walter N. LaPorte** has joined this division as director of manufacturing.

Mr. Black was formerly vice president of sales for Stepan and Mr. LaPorte comes to the company from Monsanto Chemical Company where he was manufacturing superintendent of the Boston plant.

Walter LaPorte

Dr. Lester D. Apperson has been appointed director of research for the Toilet Articles Division of the Colgate-Palmolive Company. Formerly manager of skin and oral research, Dr. Apperson will be responsible for all scientific programs at the company's Jersey City laboratories for development of new products and for improvement of existing products. Dr. Apperson joined Colgate-Palmolive in 1940 as a chemist in toilet articles research.

Dr. T. Bassiri

Edouard Beaux has joined the staff of Albert Verley & Company's subsidiary, Aromescence, Inc., Paris, France, as chief perfumer. Mr. Beaux was formerly associated with Bourjois Chanel in Paris.

Mrs. Merriom B. Pike has been named director of public relations of Ar-Ex Products Company, manufacturer of hypo-allergenic cosmetics. Mrs. Pike was previously advertising and publicity director for Lanolin Plus, Chicago.

Thomas F. LaPrelle has joined the metropolitan sales staff of Fleuroma, Inc. covering New York City and the surrounding eastern seaboard area. Mr. LaPrelle has been in the industry for several years serving as field salesman for various finished toilet goods firms.

Dr. T. Bassiri has been named staff perfumer at Fleuroma, Inc., manufacturers of perfume oils and aromatic specialties. Dr. Bassiri, internationally known in the field, has come to Fleuroma from France where he spent twenty-three years in laboratory work in chemistry, biology and particularly perfumery.

Thomas A. Wallace, Jr. will be responsible for Allied Chemical's technical program for "Genetron" in his new position of technical supervisor of this product's sales. Mr. Wallace has been with Allied Chemical's General Chemical Division for the past thirteen years.

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Also in the June issue—a Salute to The Toilet Goods Association telling of its services to the industry.

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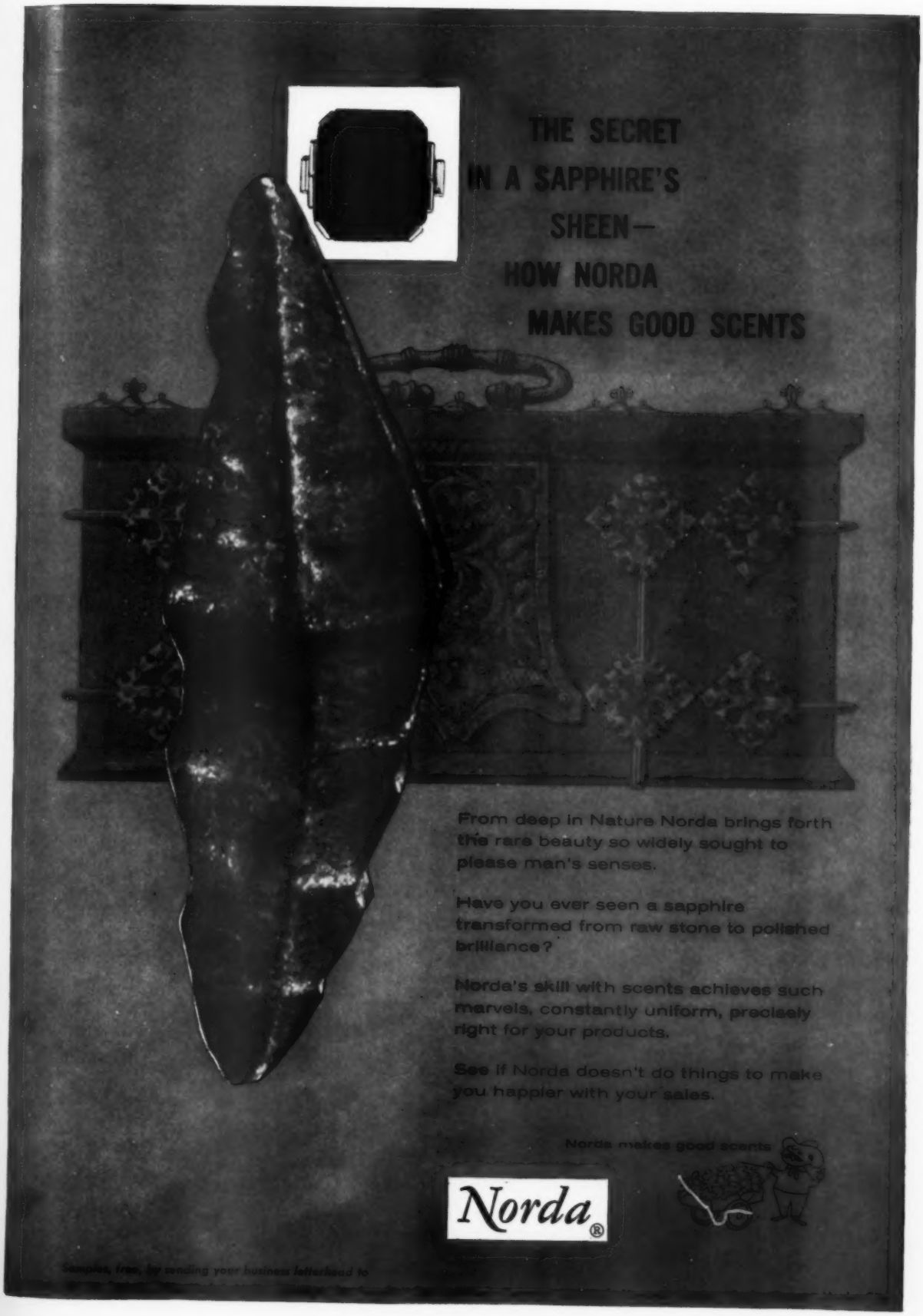
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